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POTENTIAL EMISSIONS OF HAZARDOUS ORGANIC COMPOUNDS FROM SEWAGE SLUDGE INCINERATION

by

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16. ABSTRACT

Laboratory thermal decomposition studies were undertaken to evaluate potential organic emissions from sewage sludge incinerators. Precisely controlled thermal decomposition experiments were conducted on sludge spiked with mixtures of hazardous organic compounds, on the mixtures of pure compounds in absence of sludge, and on unspiked sludge. These experiments were conducted using laboratory flow-reactor systems interfaced with a gas chromatograph or gas chromatograph-mass spectrometer for product analysis. Issues which were addressed included the effect of the sludge matrix on the thermal decomposition behavior of the hazardous sludge contaminants; potential emissions from incineration of contaminated and uncontaminated sludge; the relative contributions of the biomass and the contaminants to mass emissions in sewage sludge incineration; and potential emissions due to volatilization of organics from sludge in the drying zones of multiple hearth incinerators.

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FOREWORD

The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water systems. Under a mandate of national environmental laws, the agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. The Clean Water Act, the Safe Drinking Water Act, and the Toxics Substances Control Act are three of the major congressional laws that provide the framework for restoring and maintaining the integrity of our Nation's water, for preserving and enhancing the water we drink, and for protecting the environment from toxic substances. These laws direct the EPA to perform research to define our environmental problems, measure the impacts, and search for solutions.

The Water Engineering Research Laboratory is that component of the EPA's Research and Development Program concerned with preventing, treating, and managing municipal and industrial wastewater discharges; establishing practices to control and remove contaminants from drinking water and to prevent its deterioration during storage and distribution; and assessing the nature and controllability of releases of toxic substances to the air, water, and land from manufacturing processes and subsequent product uses. This publication is one of the products of that research and provides a vital communication link between the researcher and the user community.

This study reports on a research effort to assess the potential release of hazardous organic compounds from sludge incineration with emphasis on the identification of products of incomplete combustion.

Francis T. Mayo, Director
Water Engineering Research
Laboratory

ABSTRACT

Very little field data is available concerning organic emissions from sewage sludge incinerators. This is of particular concern because hydrophobic hazardous organic compounds, such as certain pesticides, polynuclear aromatic hydrocarbons and polychlorinated biphenyls, have been shown to partition onto the sludge during the wastewater treatment process. The environmental fate of these compounds during sewage sludge incineration is largely unknown.

Laboratory thermal decomposition studies were undertaken to evaluate potential organic emissions from sewage sludge incinerators. Precisely controlled thermal decomposition experiments were conducted on sludge spiked with mixtures of hazardous organic compounds, on the mixtures of pure compounds in absence of sludge, and on unspiked sludge. These experiments were conducted using laboratory flow-reactor systems interfaced with a gas chromatograph or gas chromatograph-mass spectrometer for product analysis. Issues which were addressed included the effect of the sludge matrix on the thermal decomposition behavior of the hazardous sludge contaminants; potential emissions from incineration of contaminanted and uncontaminated sludge; the relative contributions of the biomass and the contaminants to mass emissions in sewage sludge incineration; and potential emissions due to volatilization of organics from sludge in the drying zones of multiple hearth incinerators.

In addition to the global thermal decomposition studies described above, elementary reaction kinetic studies were conducted using a laser photolysis/laser-induced fluorescence technique. To permit in-depth understanding of some of the fundamental chemistry occurring in sewage sludge incinerators, the reaction rates of OH radicals with model chlorinated hydrocarbons were measured.

This report was submitted in fulfillment of Cooperative Agreement CR-811777 by the University of Dayton Research Institute under the sponsorship of the U.S. Environmental Protection Agency. This report covers a period from September 24, 1984 to September 23, 1986, and work was completed as of September 23, 1986.

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LIST OF ABBREVIATIONS

RCRA	Resource Conservation and Recovery Act
EPA	U.S. Environmental Protection Agency
DSS	Domestic Sewage Study
POTWs	Publicly-Owned Treatment Works
ESG	Environmental Sciences Group
UDRI	University of Dayton Research Institute
POHCs	Principal Organic Hazardous Constituents
PICs	Products of Incomplete Combustion
PCBs	Polychlorinated Biphenyls
PNAs	Polynuclear Aromatics
PCDDs	Polychlorinated Dibenzo Dioxins
PCDFs	Polychlorinated Dibenzo Furans
GC	Gas Chromatograph
GC-MS	Gas Chromatograph-Mass Spectrometer
GC/HFID	Gas Chromatograph/Hydrogen Flame Ionization Detector
Nd:YAG	Neodymium:Yttrium-Aluminum-Garnet
PMT	Photomultiplier Tube
TDU-GC	Thermal Decomposition Unit-Gas Chromatograph
FID	Flame Ionization Detector
TDAS	Thermal Decomposition Analytical System
PCP	Pentachlorophenol

SECTION 1

INTRODUCTION

There has been increasing public concern over the potential for discharge of toxic organic materials into the environment. As a result of the Hazardous and Solid Waste Amendments of 1984 to the Resource Conservation and Recovery Act (RCRA), the U.S. Environmental Protection Agency (EPA) was required to assess the number, types, and sizes of domestic sewage generators that may discharge material containing hazardous substances. The Office of Water accepted lead responsibility in preparing a report on the Domestic Sewage Study (DSS) [1].

An important result of this study was that sewage sludge generated by publicly owned treatment works could be contaminated by toxic organic compounds. Disposal of this sludge is often accomplished by incineration and the fates of these toxic organic contaminants are currently unknown. Since publicly-owned treatment works (POTWs) under existing regulations are not deemed to have received hazardous wastes, their discharge is not currently regulated. Development of possible regulations, including sewage sludge incineration, was again charged to the Office of Water.

The Environmental Sciences Group at the University of Dayton Research Institute (ESG-UDRI), was requested to conduct a laboratory study of the potential for emission of toxic organic compounds from sewage sludge incineration. The goals of this study were to generate information to guide future field studies and, most importantly, establish a data base for the development and support of possible sewage sludge incineration regulations.

Our initial evaluation identified key issues to be addressed. These include:

- What are the potential emissions of toxic organics?
- What are the contributions of the sludge matrix and the hazardous organic "contaminants" to these emissions?
- What portion of these emissions are due to undecomposed feed material versus partial decomposition products?

- What are important incineration parameters controlling hazardous organic emissions?
- Can reaction kinetics and mechanisms be understood sufficiently to predict major emissions?

We have addressed these issues in our laboratory study, the results of which are presented in the following paragraphs.

SECTION 2

CONCLUSIONS

Based on laboratory studies of the thermal decomposition of hazardous organic mixtures and sewage sludge spiked with various hazardous organic compounds, we propose the following conclusions:

- Some common hazardous organic contaminants are relatively fragile and easily destroyed, but their products of incomplete combustion pose a greater incineration challenge.
- More stable contaminants may be volatilized in the drying zone of multiple hearth incinerators and emitted with great efficiency.

The thermal decomposition behavior of common hazardous sludge contaminants differed when these Principal Organic Hazardous Constituents (POHCs) were decomposed as mixtures in a sludge matrix versus as mixtures of pure compounds. The following trends were observed for the eight POHCs tested:

- For very fragile POHCs, the sludge exerted no effect on the incinerability of the POHC.
- For POHCs of intermediate thermal stability (most of the compounds tested), the sludge appeared to decrease the incinerability of the POHC (i.e., compound was more stable in sludge).
- For very stable POHCs, the sludge increased the incinerability of the POHC (i.e., POHC was more readily destroyed in presence of sludge).
- Thermal decomposition products from the biomass itself included potentially hazardous products of incomplete combustion (PICs) which are on EPA's Appendix VIII list.
- Total mass emissions from the biomass are expected to be much greater than from trace contaminants.
- Interactions between the sludge and chlorinated contaminants may pose additional health risks in incineration of sludge from industrial sites.

SECTION 3

RECOMMENDATIONS

The results of this study have answered some very basic questions, however, some very important questions have been raised. The following additional research is recommended:

- Conduct additional laboratory studies to explain the sludge stabilization effect on hazardous organics.
- Extend laboratory testing to other sludges and contaminants.
- Extend the laboratory analysis to include identification of volatile emissions.
- Conduct laboratory analysis of the uncombusted sludge residue to determine the chemical composition of full scale particulate emissions.
- Conduct additional laboratory studies on the effects of sludge heating rate in both municipal hearth and fluidized bed systems.
- Utilize laboratory test data to guide future full-scale emissions testing and conduct correlations between predicted versus observed emissions.
- Establish a "hit list" of suspected major incinerator emissions based on laboratory data that would be the subject of full-scale compliance testing.
- Determine health effects of these emissions to compare with other sources for the establishment of a mass emissions regulatory standard.

SECTION 4

BACKGROUND

SEWAGE SLUDGE INCINERATION

While incinerators have been used to dispose of sewage sludge since the 1930's, concern regarding potential environmental insult due to organic emissions from these incinerators has developed only recently. Very little is known about organic emissions from municipal sludge incinerators, and the research program described herein was designed to begin filling in such a data base. These data are quite timely in light of the US-EPA's mission of promulgating regulations in the near future for organic emissions from sewage sludge incinerators.

Sewage sludge is a mixture of organic and inorganic materials derived from the wastewater treatment process. The primary organic constituent is the biomass, which consists of about equal amounts of protein, carbohydrates and lipids. Inorganic constituents include metal salts and oxides in the forms of silt, grit, and clay. Trace toxic metals are also present. Typical raw sewage sludge consists of about 50 to 80% volatile material (including water) and 25 to 40% organic carbon.

An estimated 1.1 million dry tons of sewage sludge are incinerated annually in the United States. It is projected that an additional 245,000 tons will be incinerated annually by the year 1990. Sewage sludge is incinerated at about 150 wastewater treatment plants having a total of about 400 incinerators. The highest concentrations of sewage sludge incinerators are found in the northeastern and Great Lakes states [2].

The 1.1 million tons of sludge incinerated annually represents about 15% of the total sewage sludge generated in the United States. Other disposal options, such as landfilling, agricultural application, and ocean disposal, have resulted in undesirable environmental consequences, especially when hazardous contaminants were present in the sludge.

Of the approximately 150 plants incinerating sewage sludge, 78% utilize multiple hearth incinerators, 16% use fluidized bed incinerators, 4% employ electric (infrared) incinerators, and 2% use other incineration technologies [2].

A diagram of a multiple hearth incinerator is given as Figure 1 [3]. This type of incinerator has been used since the 1930's for incineration of sewage sludge. The multiple hearth incinerator consists of six to twelve hearths on which the sludge progressively resides as it is dried and combusted, and the ash is finally cooled. The sludge enters the top of the incinerator and progressively drops through holes to lower hearths as it is raked and abraded by rabble arms. The rabble arms aid in mixing the sludge with oxygen and help to effect more uniform heating of the material. The sludge depth on a given hearth is about one inch, and sludge is retained in the system for 1 to 1 1/2 hours.

The multiple hearth incinerator consists of three thermal zones. In the drying zone, which exists on the upper hearths, water is gradually driven off the sludge so that the material can be combusted. The sludge is actually incinerated in the combustion zone (middle of incinerator), and the ash is cooled in the cooling zone. Temperatures in the drying zone are rather low and may cause organic components in the sludge to be volatilized without being combusted. The steady-state temperature profiles for the three multiple hearth zones are given in Table 1 [3]. Even these steady-state drying zone temperatures are too low to completely combust most organic compounds. In practice, the situation is even worse because sludge is a nonhomogeneous material and high moisture or low volatile solids content may result in lower temperatures in the drying zone. Inadequate mixing with oxygen and low gas phase residence time of desorbed organic species further inhibits combustion. In practice, odoriferous off-gases (products of incomplete combustion) are commonly emitted unless an afterburner is utilized.

TABLE 1. IDEALIZED TEMPERATURE PROFILE IN MULTIPLE HEARTH FURNACE BURNING MUNICIPAL WASTEWATER TREATMENT SLUDGE

	DRYING ZONE	BURNING ZONE	COOLING ZONE
Sludge	70°C	730°C+	200°C
Flue Gases	425°C+	830°C+	175°C+

A typical fluidized bed incinerator is depicted in Figure 2 [3]. Air enters at the bottom and flows upward into the reactor, which contains a bed of inert granular material

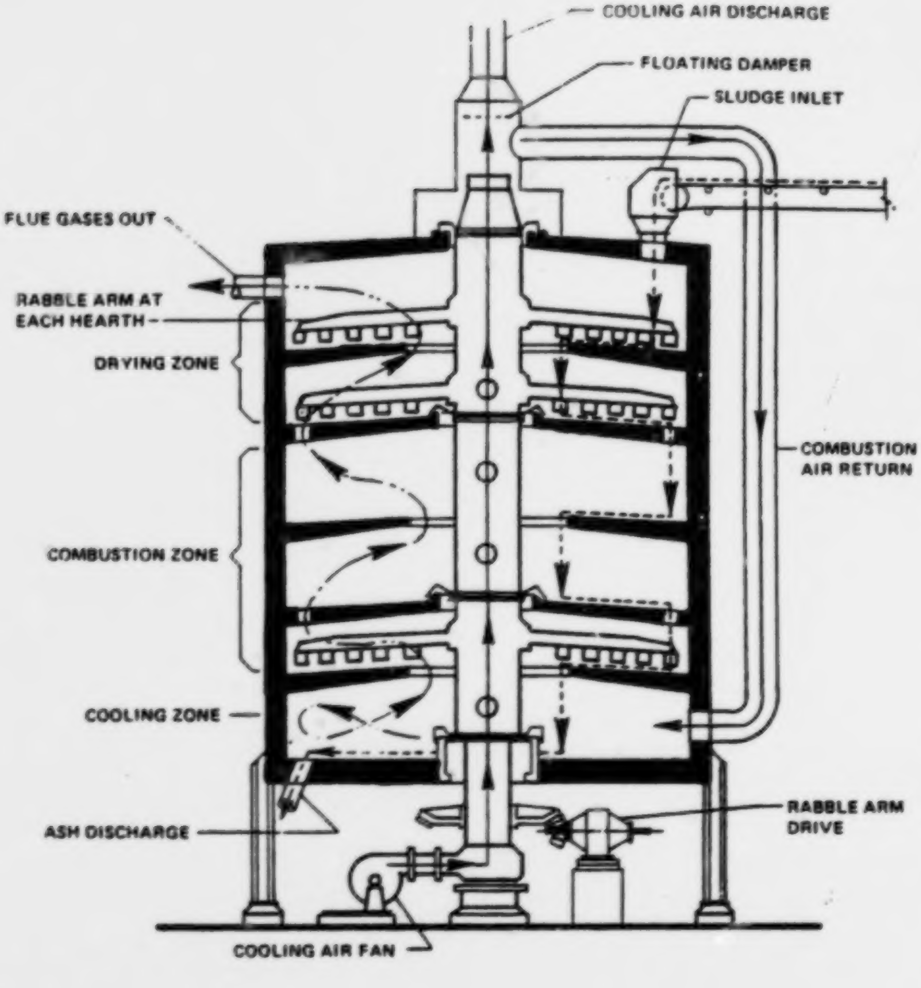

COOLING AIR DISCHARGE
FLOATING DAMPER
SLUDGE INLET
FLUE GASES OUT
RABBLE ARM AT EACH HEARTH
DRYING ZONE
COMBUSTION AIR RETURN
COMBUSTION ZONE
COOLING ZONE
ASH DISCHARGE
RABBLE ARM DRIVE
COOLING AIR FAN

Figure 1. Multiple-hearth sludge incinerator.

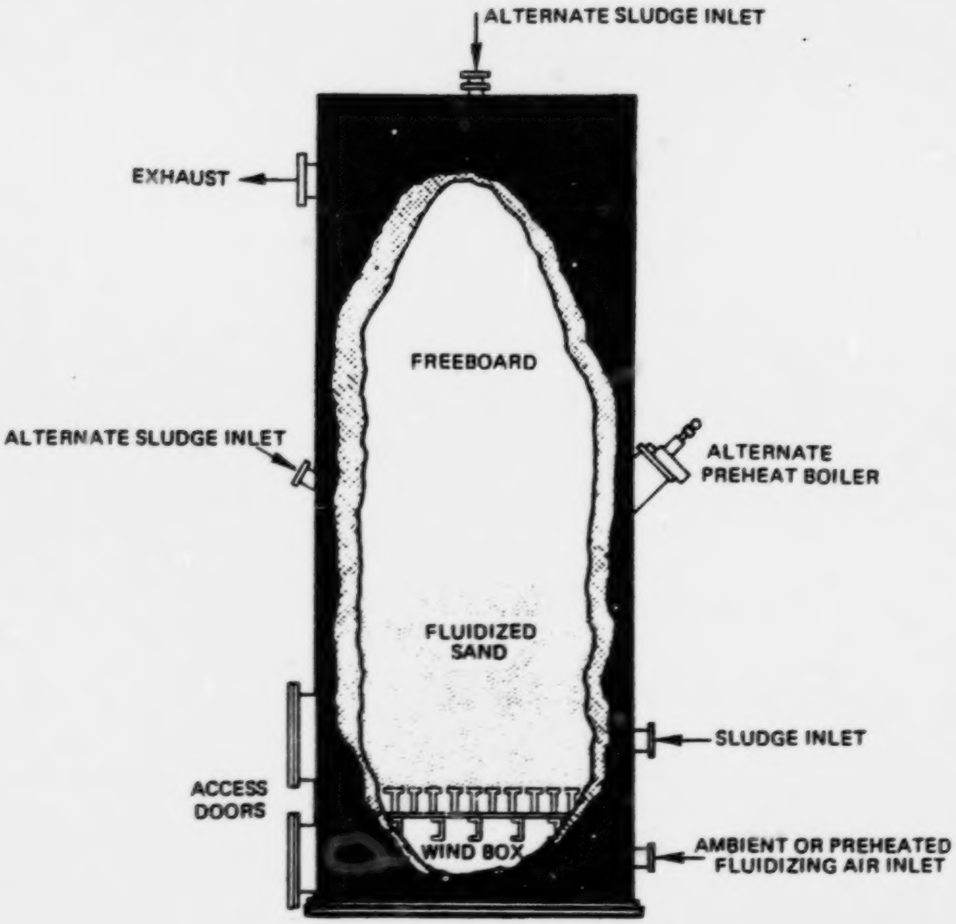

ALTERNATE SLUDGE INLET
EXHAUST
FREEBOARD
ALTERNATE SLUDGE INLET
ALTERNATE PREHEAT BOILER
FLUIDIZED SAND
SLUDGE INLET
ACCESS DOORS
WIND BOX
AMBIENT OR PREHEATED FLUIDIZING AIR INLET

Figure 2. Fluidized-bed sludge incinerator.

(typically sand). This upward flow of air causes turbulent action of the sand. The sludge is injected into the bed or freeboard zone and combustion occurs in the midst of the turbulent action of the bed. The mass of the bed is quite large in relation to the injected sludge. This affords excellent abrasive action on the sludge and maintains temperature uniformity within the reactor. Temperatures are limited by the melting point of the bed material and range from 750°C to 870°C. Temperatures do not typically vary more than 5°C throughout the bed or freeboard of the incinerator. Thus, the problems of volatilization and incomplete combustion associated with the drying zone of the multiple hearth incinerator are not expected to be as severe with the fluidized bed incinerator. A more serious problem with the fluidized bed incinerator may be entrainment of particulates in the flue gas, due to the turbulence in the bed.

Potential emissions from sewage sludge incinerators include particulates, gases such as CO, SO_x, and NO_x, trace metals, and organics. Particulates are typically emitted at levels between 10 and 400 pounds of particulates per ton of dry sludge, the exact level varying with the type and rate of feed and other operating parameters [2]. However, EPA estimates indicate that new sludge incinerators, if operated properly, could achieve the New Source Performance Standard (NSPS) of 1.3 pounds of particulates/ton dry sludge and 20% opacity (Subpart 040 CFR 60).

Sewage sludge typically contains varying concentrations of hazardous metals which may be emitted to the atmosphere during incineration. Based on recent studies in which sludges from at least 70 municipalities were analyzed for metals [4-6], the toxic metals found in highest concentrations in sludge are chromium, copper, lead and zinc. The more volatile metals, notably cadmium, lead, and zinc, are actually enriched in the particulate emissions relative to the sludge feed [7]. Metals may be adsorbed on particulates when they are emitted, or emitted as volatile salts.

While emissions from sludge incinerators of particulates, trace metals, and inorganic gases have been characterized to a moderate extent, only scanty data are available on emissions of organic compounds. It is documented however, that priority pollutants such as pesticides, polychlorinated biphenyls (PCBs), phenols, phthalates, polynuclear aromatic hydrocarbons, diazo dyes, common solvents, and nitrosamines concentrate on sewage sludge [6,8-12]. Most of these contaminants are found in concentrations of 0.1 to 100 µg/g (ppm), based on the dry weight of the sludge. Concentrations vary widely from sludge to sludge.

The source of these pollutants undoubtedly arises from industrial and household discharges of solvents, wastes, etc. The Domestic Sewage Exclusion allows hazardous wastes to be discharged to publicly-owned treatment works (POTWs) without complying with certain RCRA requirements. This hazardous waste, after being mixed with domestic sewage, is no longer legally classified as a hazardous waste. As a result of this exclusion, hazardous constituents are found in approximately 3.2 billion gallons per day of process wastewater, or approximately 12% of the total POTW flow. Approximately 3,300 metric tons of hazardous metals and 20,000 metric tons of priority organic pollutants are discharged to POTWs in the United States each year [1].

In addition to priority hazardous constituents, POTWs received significant quantities of nonpriority hazardous constituents, such as xylene, methyl ethyl ketone, etc. It is estimated that over 60,000 metric tons per year of nonpriority organics are discharged to POTWs each year [1].

Some potentially toxic organics found in sewage sludge are biodegradation products from less toxic precursors. For example, nonylphenol, a biodegradation product from nonylphenol ethoxylates (common nonionic surfactants), has been detected at levels around 1 mg/g (part-per-thousand) in sewage sludge [13-16]. Although nonylphenol is not a priority pollutant, the high concentration in sludge (10 to 10,000 times that of other organic pollutants) coupled with its toxicity to aquatic organisms (EC 50 for Daphnia Magna 0.18 mg/L), has raised concern in the United States and abroad.

Very little is known about the fate of hazardous organic constituents in sewage sludge incineration, or about total mass emissions of organics in sludge incineration. A recent Canadian study found destruction efficiencies between 64.05 and 99.98% for seven polynuclear aromatics (PNAs) in contaminated sludge which was incinerated in a multiple hearth incinerator [17]. Stack sampling from two multiple hearth and one fluidized bed incinerator revealed between 3 and 11.1 ppm hydrocarbons in the stack gas [7].

The US-EPA recently sponsored stack testing programs for chlorinated dioxin and furan emissions from three multiple hearth incinerators. Average emission levels, in g/hour, ranged from 11.6 to 780 for total polychlorinated dibenzo-p-dioxins (PCDDs), and from 90.4 to 6570 for total polychlorinated dibenzofurans (PCDFs) [18-20]. Levels did not correlate with the overall ratios of municipal to industrial contribution to the sludge, and concentrations in the sludge of well-known dioxin/furan precursors appeared to be very low. These limited data suggest that some compounds emitted from sludge incinerators may present a human health hazard, and the mechanism of their formation warrants further study.

THE LABORATORY APPROACH

Laboratory studies have been used successfully for the past ten years to examine the thermal decomposition behavior of pure compounds and hazardous waste mixtures [21-26]. Most of these laboratory studies have utilized quartz tubular flow reactors interfaced to in-line analytical instrumentation such as a gas chromatograph (GC) or a gas chromatograph - mass spectrometer (GC-MS). The thermal reactors have been designed for precise control of temperature, residence time, and atmosphere, and thus have permitted determination of the relative stabilities of organic materials as well as identifications for products of incomplete combustion (PICs).

Products of incomplete combustion form through a series of elementary chemical reactions. The thermal systems described above were not designed to probe these elementary reactions, but were rather geared toward detecting the overall decomposition, or global reactions. The distinction is illustrated in Figure 3. A laser system has recently been designed and built to study elementary reactions. These experiments provide a detailed understanding of the thermal decomposition mechanisms, which in turn permits laboratory data to be extrapolated more readily to untested materials.

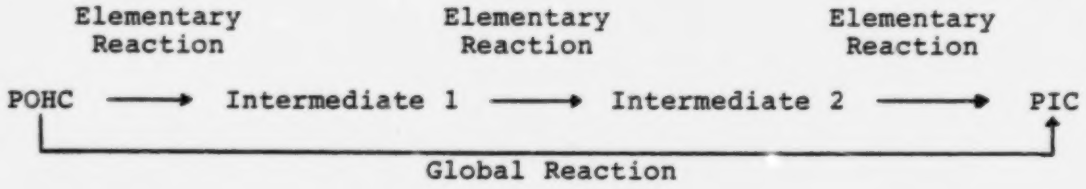


Figure 3. Distinction between elementary and global reactions.

SECTION 5

EXPERIMENTAL PROCEDURES

HYDROXYL RADICAL REACTIVITY STUDIES

OH reactivities were measured using a laser pump/laser probe technique in a specially designed and constructed atmospheric pressure high temperature optical cell. The experiment consists of five interdependent components: (1) a test cell and temperature control system, (2) the sample delivery system, (3) the pump beam laser system, (4) the probe beam laser system, and (5) the detection/measurement system.

The specially designed pyrex test cell allows gaseous reactants to be uniformly heated, irradiated with laser beams, and observed. The laminar flow characteristics in conjunction with cell design enable the gas molecules entering the cell to experience a square wave thermal pulse. A linear gas flow velocity of 4 cm/sec was chosen to ensure that each pump/probe laser pulse "sees" a fresh gas sample. This "slow flow" condition is necessary to avoid buildup of reaction products and complication of data analysis due to secondary reactions.

The gas delivery system is composed of a pyrex mixing bulb preceeded by a manifold with controlled gas inlets for nitrous oxide, water vapor, helium carrier gas, and the sample of interest. The purpose of this complex configuration is to thoroughly mix the gas constituents before they enter the cell and thus allow selectable and repeatable compositions. A sample bulb downstream of the reaction zone allows extraction of samples for gas chromatograph/hydrogen flame ionization detection (GC/HFID) testing (in the absence of OH) when thermal decomposition and/or laser-induced photolysis is a concern. The cell discharge is connected to a vacuum pump for cell cleaning and pressure control.

The pump laser is an Excimer laser (Lumonics TE-430) charged with an Argon Fluoride, ArF, mixture which lases at 193 nm. The OH radical is produced by a two step reaction process: photodissociation of nitrous oxide, N_2O, into N_2 and excited oxygen atoms, (^1D), followed by rapid reaction of oxygen atoms with water vapor to produce two OH radicals [27,28]. The experiment is run with excess water vapor ($H_2O:N_2O = 20:1$) to furnish adequate reaction sites for the oxygen atoms, to provide a clean source of OH, and to reduce the probability of oxygen atom reactions with nitrous oxide. This also allows the OH concentration to be controlled by the concentration of N_2O.

The OH radical is monitored by laser-induced fluorescence at 309.0 nm following excitation at 282.2 nm as illustrated in Figure 4. Absolute OH concentrations are determined using a three-level fluorescence model to ensure that pseudo-first-order kinetics prevail during data collection.

The probe beam system included all the components necessary to produce and deliver a 282.2 nm beam to the cell's reaction zone. The elements of this system are a Nd:YAG (Niodium-yttrium-aluminum-garnet) pulsed laser, an optically pumped dye laser, a second harmonic generator, and associated optics. The Nd:YAG, Q-switched, pulsed laser (Quanta-Ray DCR-1) is the first component in the tandem laser system. The primary beam is an infrared 1.06 μm output which is externally frequency-doubled to produce 532 nm radiation. The dye laser (Quanta-Ray PDL-2) is equipped with Rhodamine 590 dye solutions and is tuned to a visible wavelength of 584.4 nm. Upon exiting the laser, this radiation is frequency doubled (282.2 nm) by a second harmonic generating crystal for detection of OH radicals.

A quartz lens is used to image the reaction volume on the photocathode window of a photomultiplier tube, PMT (RCA 31034A). The PMT is equipped with a colored glass filter and a bandpass filter to isolate the OH fluorescence. To acquire OH signals as a function of time, a time delay system consisting of a time delay generator and silicon photodetectors for monitoring the firing of the two laser pulses was designed and constructed. An Apple IIe microcomputer generates a pulse to a delay generator circuit which interfaces with the trigger inputs of the pump and probe lasers. The delay time between the firing of the pump and probe laser is variable and controlled from the computer keyboard. A typical OH decay scan begins 1.0 ms after the pump pulse and is terminated 40 ms after the pump pulse.

Signal processing consists of conversion to a voltage source, time-discriminant multichannel amplification and analog to digital (A/D) conversion before being fed to an Apple IIe microcomputer. Automated raw data acquisition and deconvolution consists of: (1) acquiring OH (and pump and probe laser) pulses at a specified time interval (typically 100 μs) and (2) averaging OH signals over pump (and probe) pulses and normalizing to minor fluctuations in integrated laser intensities.

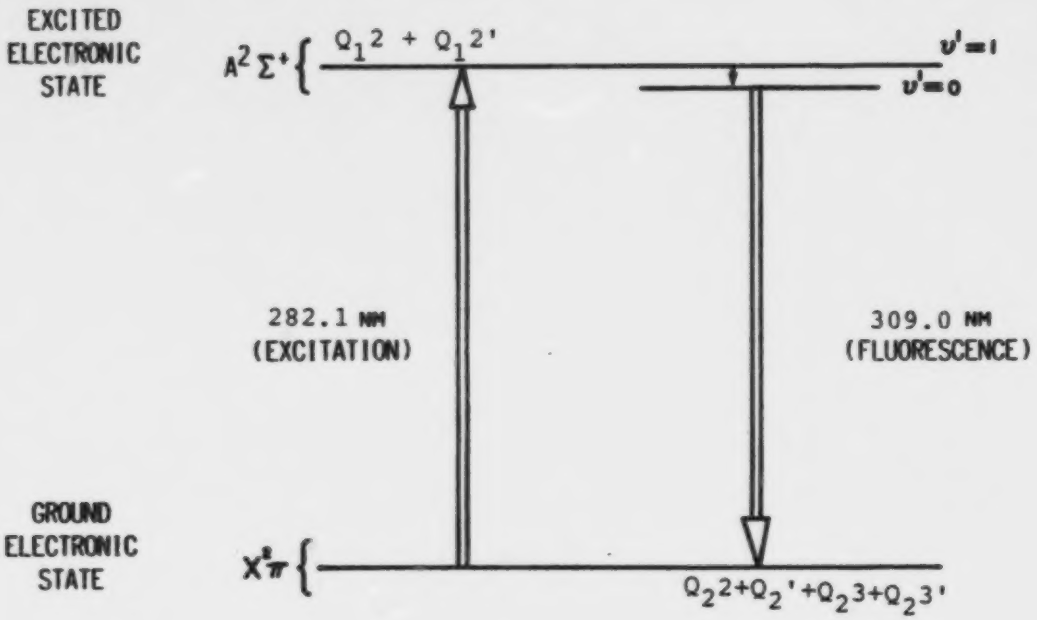

EXCITED ELECTRONIC STATE
$A^2\Sigma^+$
$Q_1 2 + Q_1 2'$
$v'=1$
$v'=0$
282.1 NM (EXCITATION)
309.0 NM (FLUORESCENCE)
GROUND ELECTRONIC STATE
$X^2\pi$
$Q_2 2+Q_2 '+Q_2 3+Q_2 3'$

Figure 4. OH energy levels pertaining to laser-induced fluorescence experiment.

A schematic of the OH generation, detection, and collection system is presented in Figure 5. A more detailed account of the theory and instrumentation for the OH reactivity studies is presented in Appendix A.

MULTIPLE HEARTH APPROXIMATION

Because both temperatures and residence times in the drying zone of the multiple hearth incinerator are relatively low, it was hypothesized that incineration efficiency would be poor in this zone. The temperature appeared to be high enough to volatilize many organic species, but not sufficiently high to effect their thermal decomposition. For this reason, an experiment was designed to determine the potential for emissions from the drying zone of a multiple hearth incinerator.

A complete description of the Thermal Decomposition Unit-Gas Chromatograph (TDU-GC) which was used for this work is provided in Appendix B, and a block diagram is reproduced as Figure 6. The TDU-GC contains two thermal zones which can be independently varied for experimental purposes - the high temperature reactor and the sample insertion region. The high temperature reactor can be maintained at constant temperatures from about 200°C up to 1000°C or greater, with residence times ranging from 0.5 to 6 seconds. When maintained in the 600°C to 900°C range, it is suitable for studying thermal decomposition in the fluidized bed incinerator or in the combustion zone of the multiple hearth incinerator. The sample insertion region, on the other hand, is programmable from ambient temperatures up to 500°C, which means that the sludge can be slowly heated as in the drying zone of the multiple hearth. The residence time of any volatilized species in this region is quite short, as is also the case with the drying zone of the multiple hearth. The thermal exposure within the drying zone of the multiple hearth incinerator was best mimicked by heating the sludge in the insertion region while maintaining the reactor at a low temperature.

To conduct this experiment, a single sludge sample was placed in the sample insertion region of the TDU-GC, and was successively heated in nitrogen over four temperature ranges, as given in Table 2. During the entire experiment, the reactor was maintained at a nondegradative temperature (300°C). While the sample was being heated over a given temperature range, any evolved species were condensed at the head of the in-line gas chromatographic column. After these species were collected, they were analyzed using programmed temperature capillary gas chromatography (GC), with flame ionization detection (FID). GC conditions were the same as those in Table 4 presented later in Section 5. Once the GC run was complete, the same sample was then heated over the next temperature range and the analytical

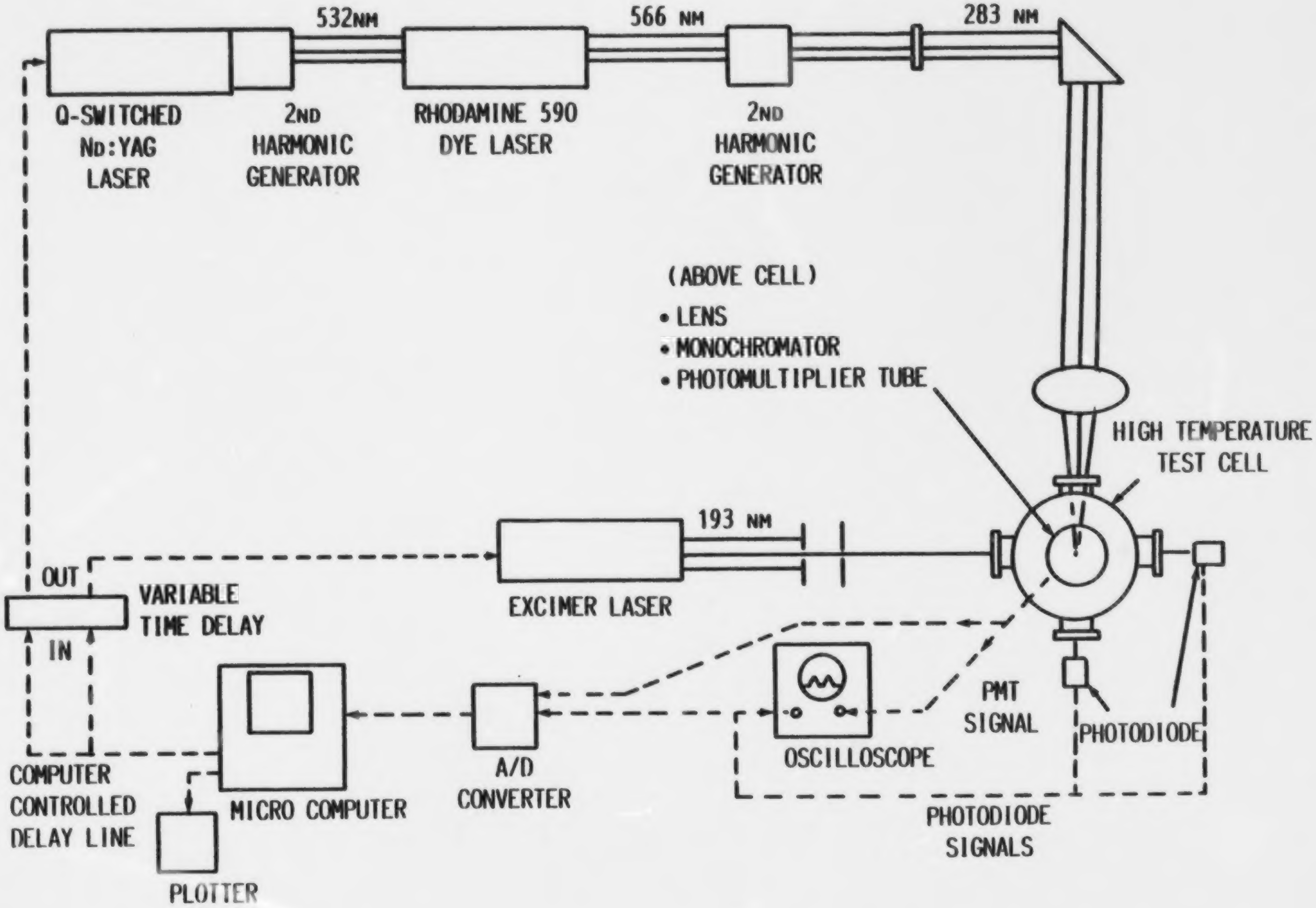

532NM
566 NM
283 NM
Q-SWITCHED
ND:YAG
LASER
2ND
HARMONIC
GENERATOR
RHODAMINE 590
DYE LASER
2ND
HARMONIC
GENERATOR
(ABOVE CELL)
• LENS
• MONOCHROMATOR
• PHOTOMULTIPLIER TUBE
HIGH TEMPERATURE
TEST CELL
193 NM
EXCIMER LASER
OUT
VARIABLE
TIME DELAY
IN
COMPUTER
CONTROLLED
DELAY LINE
MICRO COMPUTER
PLOTTER
A/D
CONVERTER
OSCILLOSCOPE
PMT
SIGNAL
PHOTODIODE
PHOTODIODE
SIGNALS

Figure 5. Schematic of hydroxyl radical generation and detection system.

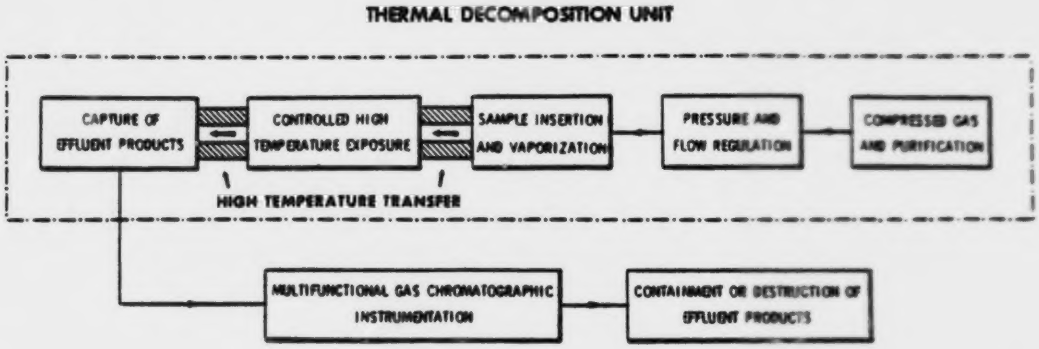

THERMAL DECOMPOSITION UNIT
CAPTURE OF EFFLUENT PRODUCTS
CONTROLLED HIGH TEMPERATURE EXPOSURE
SAMPLE INSERTION AND VAPORIZATION
PRESSURE AND FLOW REGULATION
COMPRESSED GAS AND PURIFICATION
HIGH TEMPERATURE TRANSFER
MULTIFUNCTIONAL GAS CHROMATOGRAPHIC INSTRUMENTATION
CONTAINMENT OR DESTRUCTION OF EFFLUENT PRODUCTS

Figure 6. Block diagram of TDU-GC.

TABLE 2. TEMPERATURE RANGES STUDIED FOR MULTIPLE HEARTH DRYING ZONE APPROXIMATION

Run	Temperature Range (°C)	Initial Temperature (°C)	Program Rate (°C/min)	Final Temperature (°C)	Total Desorption Time (min)
1	50-200	50	15	200	10
2	200-300	200	15	300	10
3	300-400	300	15	400	10
4	400-500	400	15	500	10

process was repeated. This procedure was repeated a total of four times, until a final temperature of 500°C was achieved. Results are given in Section 6.

A later related experiment was designed to compare potential emissions from a multiple hearth incinerator with those from a fluidized bed incinerator. Two representative aliquots from a sludge sample were heated in identical fashions in the sample insertion region. Desorbed species were passed through the reactor, which was held at either 300°C (multiple hearth approximation) or 800°C (fluidized bed approximation). The reactor effluent was trapped and analyzed as before. Results are again presented in Section 6.

THERMAL DECOMPOSITION OF SPIKED SLUDGES AND SPIKING MIXTURES

The majority of this program was directed towards studying the thermal decomposition of common sewage sludge contaminants, as well as identification of products of incomplete combustion (PICs) from contaminated sewage sludge. To achieve these goals, thermal decomposition studies were conducted on the Thermal Decomposition Unit-Gas Chromatographic (TDU-GC) system and the Thermal Decomposition Analytical System (TDAS). Block diagrams of these systems are given in Figures 6 and 7, respectively. Both systems include thermal decomposition units in which temperature, atmosphere, and mean residence time can be precisely controlled. In the case of the TDU-GC, this thermal unit is interfaced with an in-line gas chromatograph (GC), while in the case of the TDAS, the analytical instrumentation is an in-line gas chromatograph-mass spectrometer (GC-MS). Details concerning these systems are given in Appendix B.

Thermal decomposition studies were conducted on a relatively clean sludge spiked with mixtures of contaminants, on mixtures of pure contaminants (without sludge), and on unspiked sludge. Contaminants were studied in mixtures rather than as pure compounds so that a number of compound classes could be investigated within the constraints of the program.

Variables other than sample matrix which were investigated in these studies included gas phase temperature (300°C to 1000°C) and oxygen level (air for combustion studies and nitrogen for pyrolytic studies). For spiked sludges and mixtures of pure compounds, the TDU-GC was used to generate thermal decomposition curves as a function of reactor temperature and oxygen level. The TDAS was then used to identify PICs by selecting reactor temperatures which, based upon TDU-GC data, would yield the majority of the PIC identifications. The unspiked sludge was studied using the TDAS only, since there were no thermal decomposition profiles to generate.

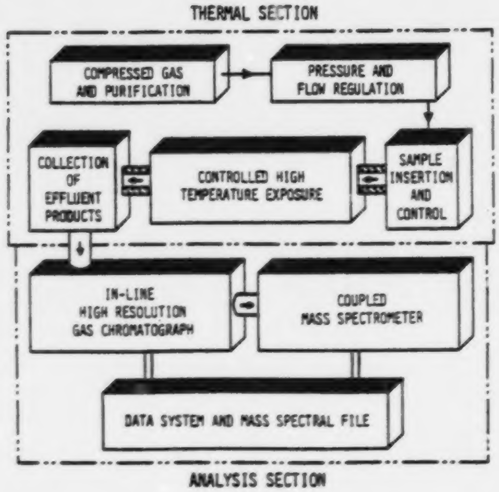

THERMAL SECTION
COMPRESSED GAS AND PURIFICATION
PRESSURE AND FLOW REGULATION
COLLECTION OF EFFLUENT PRODUCTS
CONTROLLED HIGH TEMPERATURE EXPOSURE
SAMPLE INSERTION AND CONTROL
IN-LINE HIGH RESOLUTION GAS CHROMATOGRAPH
COUPLED MASS SPECTROMETER
DATA SYSTEM AND MASS SPECTRAL FILE
ANALYSIS SECTION

Figure 7. Block diagram of TDAS.

Common classes of sludge contaminants are listed in Table 3, along with the representative of each class which was actually spiked onto sludge for thermal decomposition testing. With the exception of nonylphenol, all the compounds were spiked onto the sludge as mixtures. Technical grade nonylphenol was in itself a mixture of 4-nonylphenol and 2-nonylphenol isomers, as well as some octylphenols and decylphenols, and further complication of this material was not desirable. The other compounds were studied as mixtures designated as Composite A and Composite B. Their compositions were as follows:

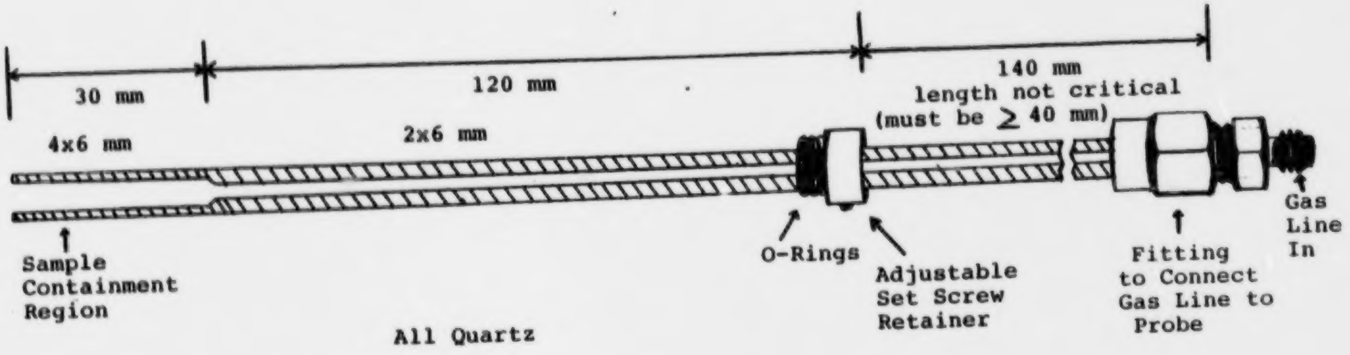
Composite A	Composite B
heptachlor	butyl benzyl phthalate
pentachlorophenol	2,3',4,4',5-pentachlorobiphenyl
diphenylnitrosamine	azobenzene
pyrene	

Sewage sludge used for these studies was a filter cake sludge containing 17% solids, and was obtained from the City of Miamisburg Wastewater Treatment Plant in Miamisburg, Ohio. This sludge was not adequately dewatered for efficient incineration, but was otherwise similar in composition to sludges which are incinerated. The sludge was spiked on a wet weight basis at about 1 mg/g with the organic components, except nonylphenol, which was spiked at 10 mg/g. These levels are at least an order of magnitude greater than those typically found in "real world" sludges, but such spike levels were required to minimize interferences on the TDU-GC from the sludge matrix. The spikes were applied as acetone solutions, and the acetone was subsequently allowed to evaporate. It should be noted that highly volatile sludge components were unavoidably lost at this stage. The alternative, permitting the acetone to remain on the sludge would have produced substantial alterations in the matrix. All sludge samples were "diluted" with high purity silicon dioxide (Aldrich, 99.999%), to facilitate weighing of samples on an analytical balance.

Samples were inserted into the instrument using quartz probes. A diagram of the probe designed for sludge samples is shown in Figure 8. Sludge samples were retained between plugs of quartz wool in quartz cartridges which fit snugly into the probe. To prevent contamination from laboratory air, these cartridges and the quartz wool were stored in an oven at 400°C until just prior to use. Solutions of pure mixtures were prepared in acetone and were applied in 5 to 10 μL aliquots to a quartz solids probe. The solvent was permitted to evaporate prior to introduction of the sample into the system. The various probes and the analytical system were thermally desorbed each day before use.

TABLE 3. COMMON CLASSES OF SEWAGE SLUDGE CONTAMINANTS AND SPECIFIC COMPOUND SPIKED ONTO SLUDGE FOR THERMAL DECOMPOSITION TESTING

Class	Specific Compound
Chlorophenol	Pentachlorophenol
Nitrosamine	Diphenylnitrosamine
PNA	Pyrene
Pesticide	Heptachlor
Nonylphenol	Nonylphenol
Phthalate	Butyl benzyl phthalate
PCB	2,3',4,4',5-Pentachlorobiphenyl
Diazo dye	Azobenzene



30 mm
120 mm
140 mm
length not critical
(must be ≥ 40 mm)
4x6 mm
2x6 mm
Sample Containment Region
O-Rings
Adjustable Set Screw Retainer
Fitting to Connect Gas Line to Probe
Gas Line In
All Quartz

Figure 8. Probe used to introduce sludge samples.

A thermal decomposition run was initiated by inserting the sample, contained in the sludge probe, into the sample insertion region. After allowing laboratory air to be purged from the system, the insertion region was programmed from 50°C to 200°C at 15°C/min. (Some early work involved heating the insertion region to 300°C, but this procedure was modified due to system contamination.) During sample heating, the vaporized sample components were conveyed into the reactor using either nitrogen or air. The reactor temperatures were varied over the range of 300°C to 1000°C, and a 2 second gas-phase mean residence time was maintained in the reactor. The reactor effluent (both undecomposed parents and products of incomplete combustion) was trapped at the head of the in-line gas chromatographic column. After purging the system with a helium carrier gas, the GC was programmed to elute the trapped species, which were detected using an FID detector for the TDU-GC, or a mass spectrometer for the TDAS. Analytical instrumentation conditions for the TDU-GC and the TDAS are given in Tables 4 and 5, respectively. Frequent method blanks and duplicates were run to ensure the integrity of the data.

THERMAL DECOMPOSITION OF RELATED PURE COMPOUNDS

To gain a better fundamental understanding of some of the thermal decomposition studies with spiked sludge, additional studies were undertaken for pentachlorophenol and phenol as pure compounds. Pentachlorophenol (PCP) was investigated because it was a member of the Composite A spiking mixture, and phenol was investigated because it was a major decomposition product from nonylphenol (but was not a product of PCP decomposition). It was desired to compare the thermal decomposition behavior of the unsubstituted phenol with those of the chlorinated phenol (PCP) and the alkylphenol (nonylphenol).

Pentachlorophenol was studied using both the TDU-GC and the TDAS. Thermal decomposition profiles were generated in both air and nitrogen, and products of incomplete combustion were identified. Thermal decomposition profiles were generated for phenol using the TDU-GC, but PICs were not identified due to time constraints. Instrument conditions were the same as those described earlier in Section 5 for the pure mixtures.

TABLE 4. GC CONDITIONS FOR TDU-GC

GAS CHROMATOGRAPH: Varian 4600

DETECTOR: Hydrogen flame ionization (HFID)

COLUMN: DB-5 fused silica capillary column (J&W) 15m x 0.25 mm ID x 0.25 μ film thickness

OVEN PROGRAM: Hold at initial temperature of 35°C (for spiked sludge) or -40°C (for pure mixtures) for 1 min.; program at 10°C/min to 300°C; hold 10 min. at final temperature

CARRIER GAS: Helium

DETECTOR TEMPERATURE: 300°C

TABLE 5. GC-MS CONDITIONS FOR TDAS

GAS CHROMATOGRAPH: Varian 2400

MASS SPECTROMETER: LKB 2091 (Magnetic)

COLUMN: DB-5 fused silica capillary column (J&W), 30 m x 0.25 mm ID x 0.25 μ film thickness

OVEN PROGRAM: Initial temperature of 35°C (for spiked sludge) or -40°C (for pure mixtures); program at 10°C/min to 300°C; hold 10 min at final temperature

CARRIER GAS: Helium

GC-MS TRANSFER LINE TEMPERATURE: 250°C

GC-MS INTERFACE: glass jet separator

SOURCE TEMPERATURE: 250°C

IONIZATION MODE: electron impact

ACCELERATING VOLTAGE: 3.5 kV

TRAP CURRENT: 50 μA

ELECTRON ENERGY: 70 eV

SCAN RANGE: 40 to 490 amu

SCAN SPEED: 2 sec/decade

SECTION 6

RESULTS AND DISCUSSION

HYDROXYL RADICAL REACTIVITY STUDIES

For the combustion of hydrocarbons, OH radicals are the dominant reactive species under all but the most fuel-rich environments [29]. Although it is recognized that chlorine atom reactivity may be important for chlorinated hydrocarbons such as those produced as PICs in the thermal degradation of contaminated sewage sludge, OH reaction kinetics are considered most significant with respect to the oxidative destruction of these materials. Since there is a general paucity of data on OH-chlorocarbon reactions and data are practically non-existent at the high temperatures which simulate incinerator conditions, the high temperature elementary reaction rates of OH radicals with select chlorocarbons was studied for this program via a laser photolysis/laser-induced fluorescence technique [27,28].

The experimental approach which was used allows the generation and detection of OH radicals in a "clean" environment where essentially only OH-chlorocarbon reactions can occur. This eliminates the complexities of rate constant determinations in multireaction media such as shock tubes, flames, and flow reactors. The experimental design is controlled by the following kinetic scheme for the destruction of molecule A:

$$-d[A]/dt = k_1[A] + k_2[A][O_2] + \sum_i k_i[A][r_i]$$

where: $k_1[A]$ is the rate of unimolecular decomposition of A, $k_2[A][O_2]$ is the bimolecular reaction rate of A with molecular oxygen, and $k_i[A][r_i]$ represents bimolecular reaction rates with other reactive species.

By design, this experiment is conducted with OH concentrations in excess of the other reacting species to ensure that pseudo-first order kinetics are appropriate for the rate determination. The general kinetic expression can be simplified to consider only the OH radical reaction. Since A is in large excess (x 100-1000), the change in concentration of OH is measured over time. The first order reaction rate of OH with A can be expressed as:

$$-d[OH]/dt = -k[A_o][OH] - k_d[OH]$$

where: [OH] is the concentration of OH at time t, $[A_o]$ is the initial concentration of chlorocarbon A which remains constant relative to [OH], k is the rate constant for attack of OH with chlorocarbon, and k_d is the rate constant for the reduction of OH by diffusion from the reaction volume and by reactions with background impurities. Integration of this expression yields the expression:

$$[OH]/[OH]_o = \exp\{(-k[A_o] + k_d)t\}.$$

Defining the pseudo-first order rate constant:

$$k' = k[A_o] + k_d$$

and the fraction of OH remaining at time t:

$$f_r = [OH]/[OH]_o$$

results in the expression:

$$\ln(f_r) = k't.$$

The slope of a plot of ln (f_r) versus t yields the rate constant k'. A plot of k' versus $[A_o]$ yields the desired elementary rate constant for the reaction of OH with various chlorocarbons. Thus by monitoring relative concentrations of OH over time, the reaction rate of OH radicals with chlorocarbons can be determined.

The chloromethanes were chosen as model chlorocarbon compounds for this initial study based on the following observations with respect to the oxidative thermal degradation of contaminated sewage sludge:

(1) Of all contaminated sludges studied, only pentachlorophenol and pentachlorobiphenyl contaminants exhibited destruction efficiencies less than 99.9% at temperatures less than 700°C;

(2) PIC classes produced from interaction of sludge matrix and spiked contaminants which will most seriously affect incinerator efficiency (defined by being detectable at temperatures greater than 800°C) are chlorinated hydrocarbons, aromatic hydrocarbons, and PNAs.

Figure 9 presents a typical OH decay profile averaged over 5 laser pulses per time delay interval. This decay is representative of the exponential decrease in OH concentration with an excess of CH_2Cl_2 present at 299 K. The OH decay shown has also been normalized to the simulation of the pump and probe beam intensities at each time delay interval. This effectively smooths the OH decay curve for random fluctuations in laser powers.

Pseudo-first order rate constants have been generated for all the chloromethanes over a temperature range of 299 to 774 K. Samples were prepared by injection of specific quantities of liquid (and gas for CH_3Cl) into a one liter glass bulb such that the partial pressure of each sample was 200 torr. Chloromethane concentrations within the reaction volume were varied from $4x10^{13}$ to $57x10^{13}$ molecules/cm^3 for each rate determination. A three-level fluorescence model predicted the OH concentration within the reaction volume to be 1x10" to 2x10" molecules/cm^3. Thus, it was valid to assume pseudo-first order kinetics in data interpretation.

Table 6 presents bimolecular rate constants for reactions of OH radicals with the chloromethanes over a temperature range of 573 to 773 K. A statistical propagation of error analysis [30], has been applied to the data collection procedure (see Appendix D) with the results presented in Table 6. With minor exceptions, good precision is indicated as standard deviations in the rate constants are generally less than 10% of the measured value. The temperature dependence of the bimolecular rate constants have been evaluated with weighted least-squares algorithms [5] in relation to the Arrhenius expression:

$$k = A \exp [-Ea/RT]$$

and the three-parameter non-Arrhenius expression:

$$k = BT^n \exp [E/T]$$

where A is the preexponential factor, B is the temperature dependent preexponential factor, n is a constant (typically on the order of unity for gas-phase reactions), Ea is activation energy, and E is temperature-dependent activation energy.

The data analyzed in this manner always exhibited non-Arrhenius kinetics with the results presented in Table 7.

The rate data indicated relative OH reactivities for the chloromethanes to be:

$$CHCl_3 \geqslant CH_2Cl_2 > CH_3Cl >> CCl_4.$$

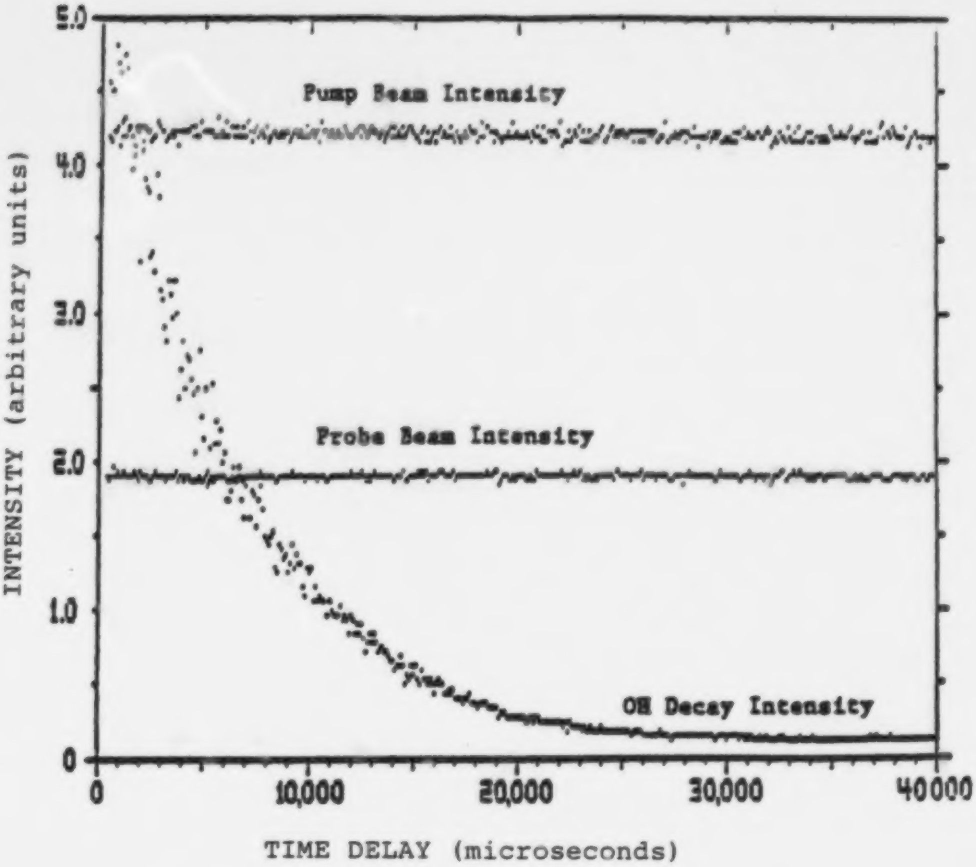


Figure 9. OH decay in the presence of excess CH_2Cl_2. Also shown are relative pump and probe beam intensities. T = 299 K, p ≈ 1 atm.

TABLE 6. CHLOROMETHANE-OH RATE CONSTANTS

Reactant	k(10^{13}cm^3/molec-s)	T(K)
CH_3Cl	8.83±0.296[a]	578
CH_3Cl	15.96±1.31	687
CH_3Cl	24.97±2.25	776
CH_2Cl_2	11.12±0.590	580
CH_2Cl_2	19.83±2.94	674
CH_2Cl_2	33.26±4.09	773
$CHCl_3$	14.07±1.60	571
$CHCl_3$	20.00±1.46	680
$CHCl_3$	31.73±1.81	772
CCl_4	1.65±0.056	614
CCl_4	3.54±0.050	773
CCl_4	5.12±0.800	782

---

[a] One standard deviation in data.

TABLE 7. NON-ARRHENIUS PARAMETERS FOR CHLOROMETHANE-OH REACTIONS

Reactant	B(cm^3/molec-s)	n	E(cal/mole)	T Range (K)
CH_3Cl	5.89±1.22[a]x10^{-21}	3.0	-145±59[a]	296-776
CH_2Cl_2	5.14±0.98x10^{-21}	3.0	75±59	298-773
$CHCl_3$	8.38±0.45x10^{-21}	3.0	-70±21	298-772
CCl_4	4.56±0.80x10^{-22}	3.0	331±67	296-782

---

[a] One standard deviation in data.

The high temperature relative reactivities for CH_3Cl, CH_2Cl_2, and $CHCl_3$ are in accord with their gas-phase thermal stabilities under oxidative conditions [31]. In other words, OH reactivity increases with increasing Cl substitution for the chloromethanes. This indicates that OH reactivity is more sensitive to the ease of hydrogen atom abstraction (which increases as the Cl atom substitution increases) as compared to the total number of abstractable H atoms present. If we extend this hypothesis to the limit of perchlorinated compounds, these results indicate a much smaller OH reactivity as compared to any of the hydrogen-containing chloromethanes. Although the C-Cl bond in CCl_4 is weaker than any C-H bond in the remaining chloromethanes, the large endothermicity of this reaction due to the low stability of HOCl formation results in a relatively high energy reaction pathway.

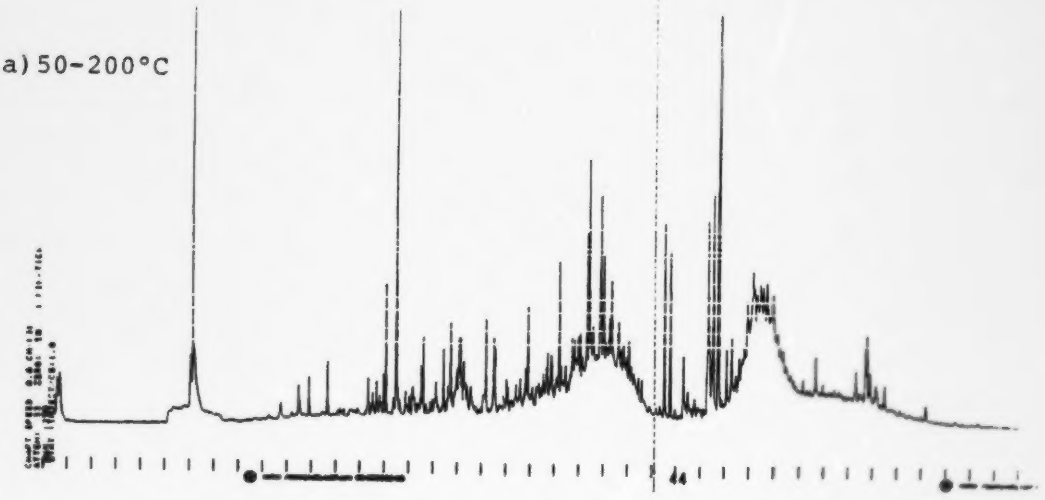
Extrapolating these results to the types of PICs produced in the oxidative degradation of contaminated sewage sludge, perchlorinated hydrocarbons such as C_2Cl_2, C_2Cl_4, C_3Cl_4, and C_4Cl_4O should prove difficult to incinerate as compared to their hydrogen containing analogs (i.e., C_2HCl, C_2HCl_3) due to the lack of abstractable hydrogen atoms. Additional PICs believed to form from the sludge matrix such as simple aromatics (i.e., benzene, toluene, styrene) should prove difficult to incinerate as compared to their chlorinated analogs because of the larger C-H bond energies. The same reasoning can be applied to chlorinated and non-chlorinated PNAs which form as PICs at extremely high temperatures. Recent OH reactivity studies with non-chlorinated aromatics [32-35] indicate that oxidation rates should be highest for compounds having the highest bound hydrogen content. For some of the single-ring aromatics and PNAs produced as PICs in this study, it may be predicted that the oxidation rates increase in the order:

$$C_6H_6 < C_7H_8 < C_{10}H_8 < C_8H_8 < C_{12}H_{10} < C_{16}H_{10}.$$

The relative combustion rates for aromatic fuels with the same number of hydrogen atoms may be estimated based on relative C-H bond strengths.

MULTIPLE HEARTH APPROXIMATION

Results of the experiment designed to approximate the thermal desorption/decomposition in the upper hearths of a multiple hearth incinerator are shown in Figure 10. The majority of the volatile sludge components desorbed during the initial program step between 50 and 200°C. Significant residuals also desorbed in the 200 to 300°C and the 300 to 400°C ranges, but a marked decrease in desorbed organics was seen between 400 and 500°C. Overall these chromatograms clearly illustrate the potential for major emissions from


a) 50-200°C

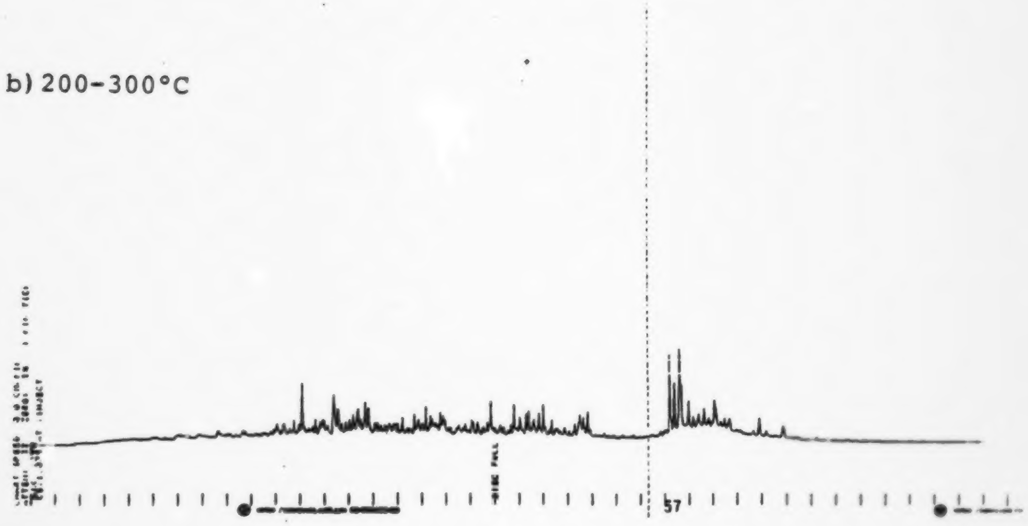
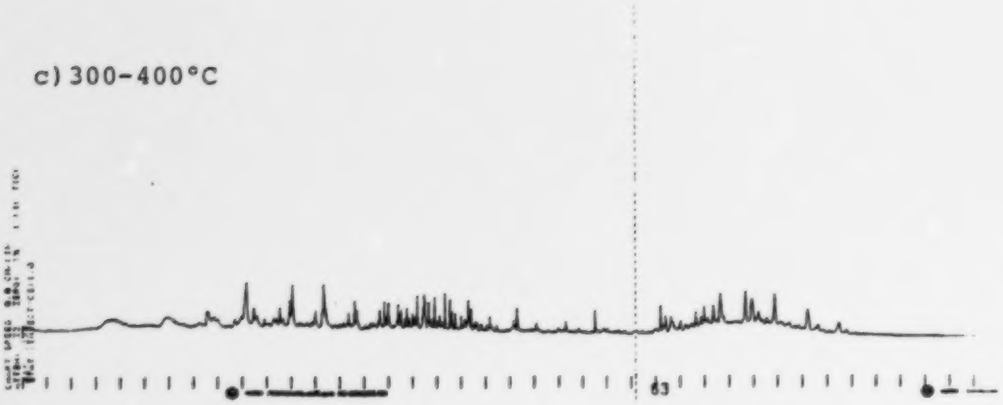

b) 200-300°C

Figure 10. Chromatograms of organics desorbed from sludge in various sample insertion region temperature ranges.

c) 300-400°C



d) 400-500°C

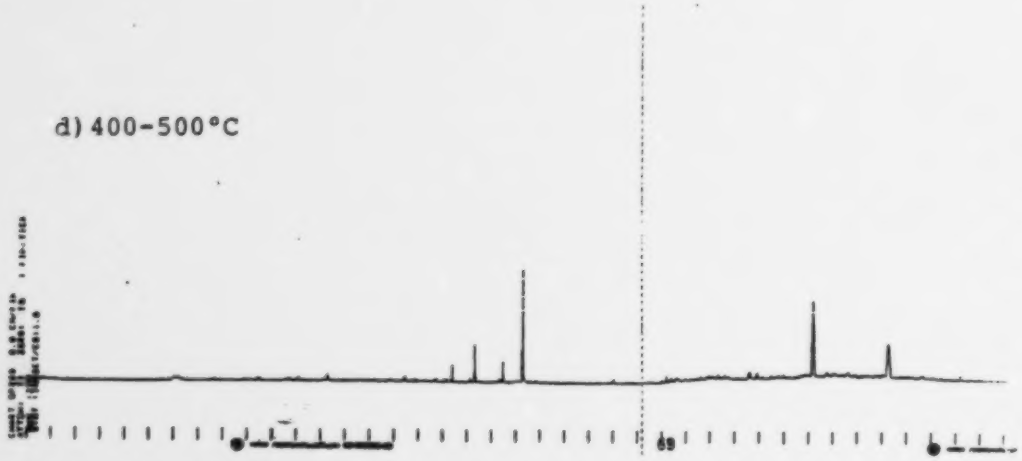


Figure 10. (Continued)

volatilization and/or incomplete combustion of sludge components in the drying zone of the multiple hearth incinerator.

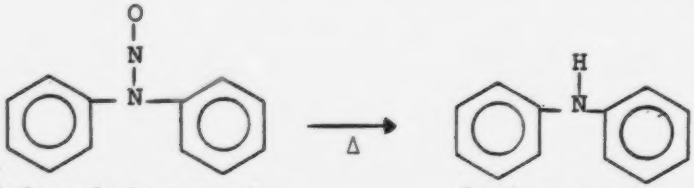
A comparison of potential emission levels from the multiple hearth versus the fluidized bed incinerator is shown as Figure 11. The top chromatogram depicts volatile species desorbed from the sludge and conveyed through the reactor at 300°C, while the bottom chromatogram shows the remaining species after these volatilized organics have been subjected to an 800°C reactor temperature. While the thermal conditions in the top chromatogram approximate those in the drying zone of the multiple hearth incinerator, those in the bottom chromatogram are more characteristic of the thermal regime in the fluidized bed incinerator. In the latter incinerator, vaporized organics immediately experience temperatures of approximately 800°C. (It should be noted, however, that the sludge heating rate in the fluidized bed incinerator is much faster than that used for these experiments.) Figure 11 indicates that more than 90% of the volatile sludge components are decomposed at 800°C, resulting in a chromatographic pattern of greatly reduced complexity. This indicates that the thermal regime of the fluidized bed incinerator is much less likely than that of multiple hearth to lead to major gaseous organic emissions. Potential emissions of organics on particulates have not been addressed in this study.

THERMAL DECOMPOSITION OF SPIKED SLUDGES AND SPIKING MIXTURES

Thermal Decomposition Profiles for Common Sludge Contaminants

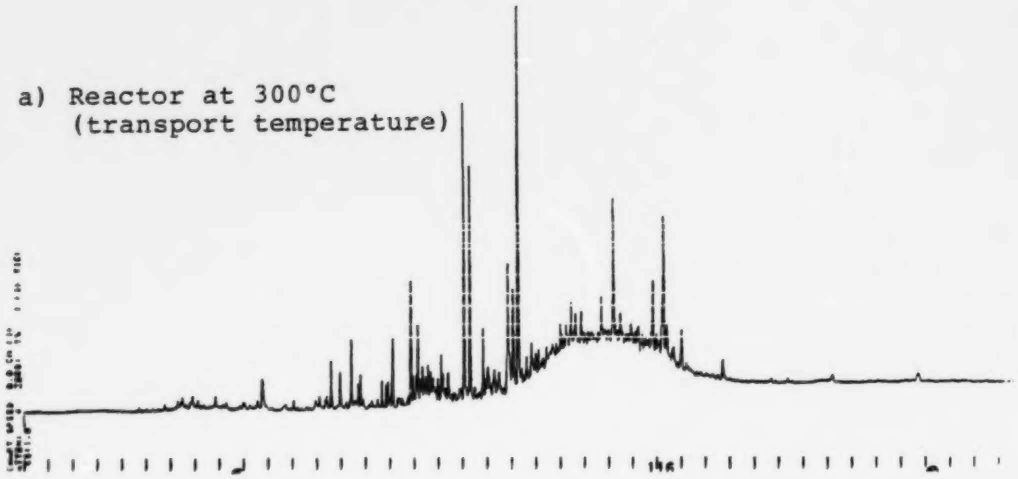
In this section, data are presented on the thermal decomposition of eight classes of sewage sludge contaminants. The classes include chlorophenols, phthalates, nitrosamines, polynuclear aromatic hydrocarbons, polychlorinated biphenyls, diazo dyes, pesticides, and nonylphenols. This section describes the rates of thermal decomposition of a representative member of each of these eight classes of compounds.

The representative nitrosamine, diphenylnitrosamine, was quantitatively converted to diphenylamine at temperatures less than 275°C.



Diphenylnitrosamine Diphenylamine

a) Reactor at 300°C
(transport temperature)



b) Reactor at 800°C

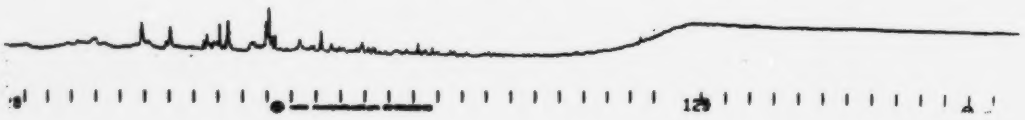


Figure 11. Chromatograms of organics a) desorbed from sludge versus b) desorbed from sludge and then thermally decomposed at 800°C.

The subsequent decomposition of the diphenylamine was then profiled as if it were the parent material. Many of the nitrosamines are too thermally labile to be analyzed by gas chromatography and would be expected to decompose at low temperatures.

A problem with thermal lability was also encountered for the diazo dyes, which require liquid chromatographic analysis. Azobenzene, a chromatographable subunit of diazo dyes, was run as a surrogate for these materials. Many diazo dyes would be expected to be readily destroyed during incineration.

The nonylphenol used for this program was a technical grade which would be similar to that used commercially. This standard contained a mixture of nonylphenol isomers, as well as some decylphenols and octylphenols. Since all the isomers decomposed at virtually identical rates, the sum of the largest three peaks was profiled for the decomposition experiments.

Thermal decomposition profiles for eight POHCs which were studied extensively for this program are shown in Figures 12 through 19. These curves depict thermal decomposition as a function of both matrix (spiked sludge versus spiking composite) and atmosphere (nitrogen versus air) Some interesting effects can be observed from these profiles. First, as expected, the materials tested were more stable in nitrogen than in air, and the magnitude of the atmosphere effect varied with the compound. The compounds in which the atmosphere had little effect were those in which lower-energy decomposition pathways were available. Secondly, the presence of the sludge had varying effects on the decomposition rate of the POHCs. The effects of the sludge on apparent thermal stability of the POHCs is summarized in Table 8.

For a given atmosphere, the diphenylamine, nonylphenol, pentachlorophenol, and azobenzene were apparently more stable in the sludge matrix than in the mixtures. There are three possible explanations for this behavior. The trivial explanation is that there was a coeluting peak in the TDU-GC data which caused the compound to appear more stable. Interferences would be more likely to occur in the spiked sludge matrix than in the mixtures because the sludge produces a very complex chromatogram. Mass spectral data indicate, for example, that the data points at 800°C and 1000°C on the pentachlorophenol curve for the spiked sludge in nitrogen were probably elevated due to an interference. However, in the low-temperature portion of this and many of the other curves, interferences are not expected to be significant because greater than 10% of the parent remains, and the signal produced by such a chromatographic peak is generally significantly

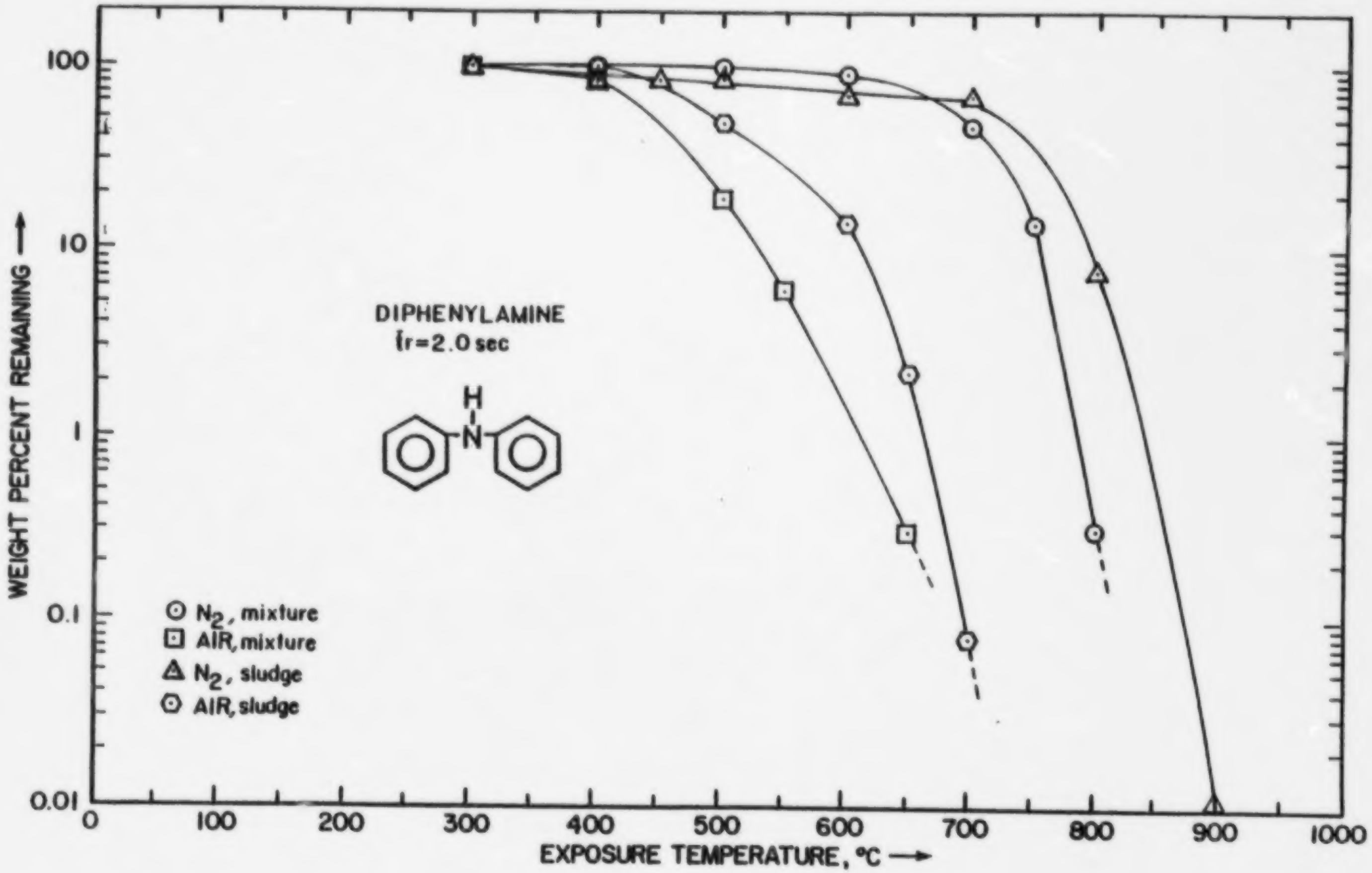


Figure 12. Thermal decomposition profiles for diphenylamine.

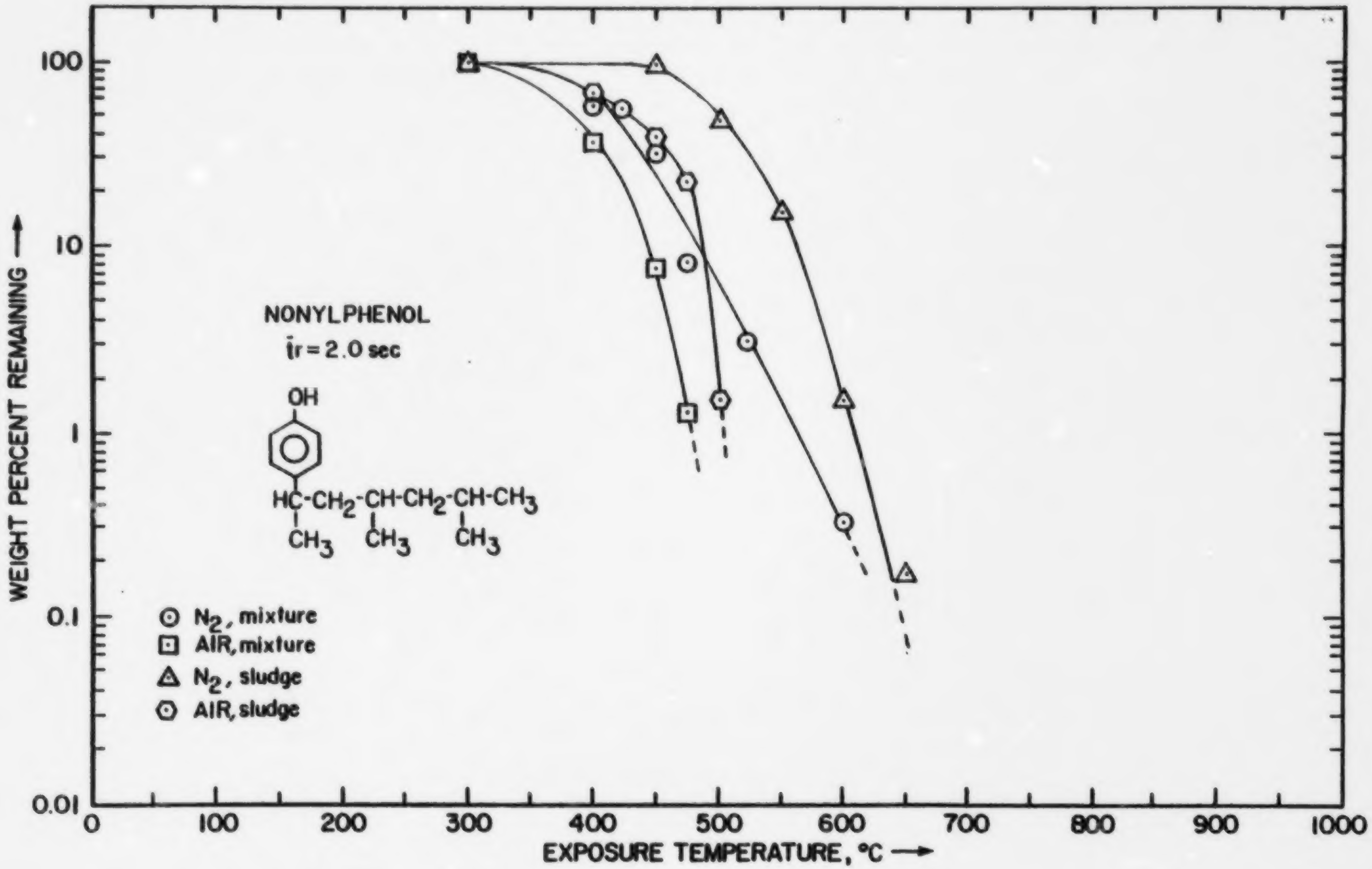


Figure 13. Thermal decomposition profiles for nonylphenol.

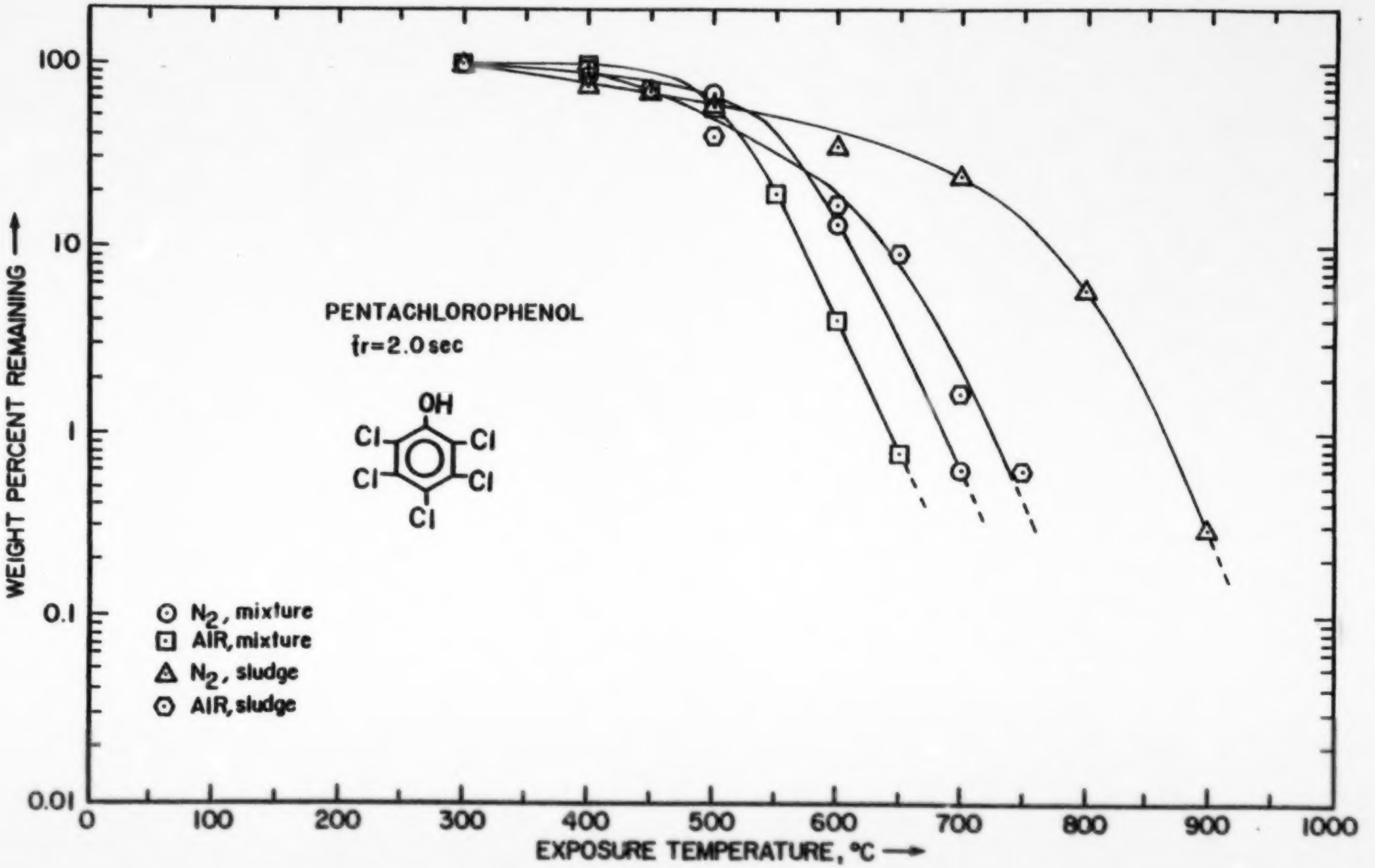


Figure 14. Thermal decomposition profiles for pentachlorophenol.

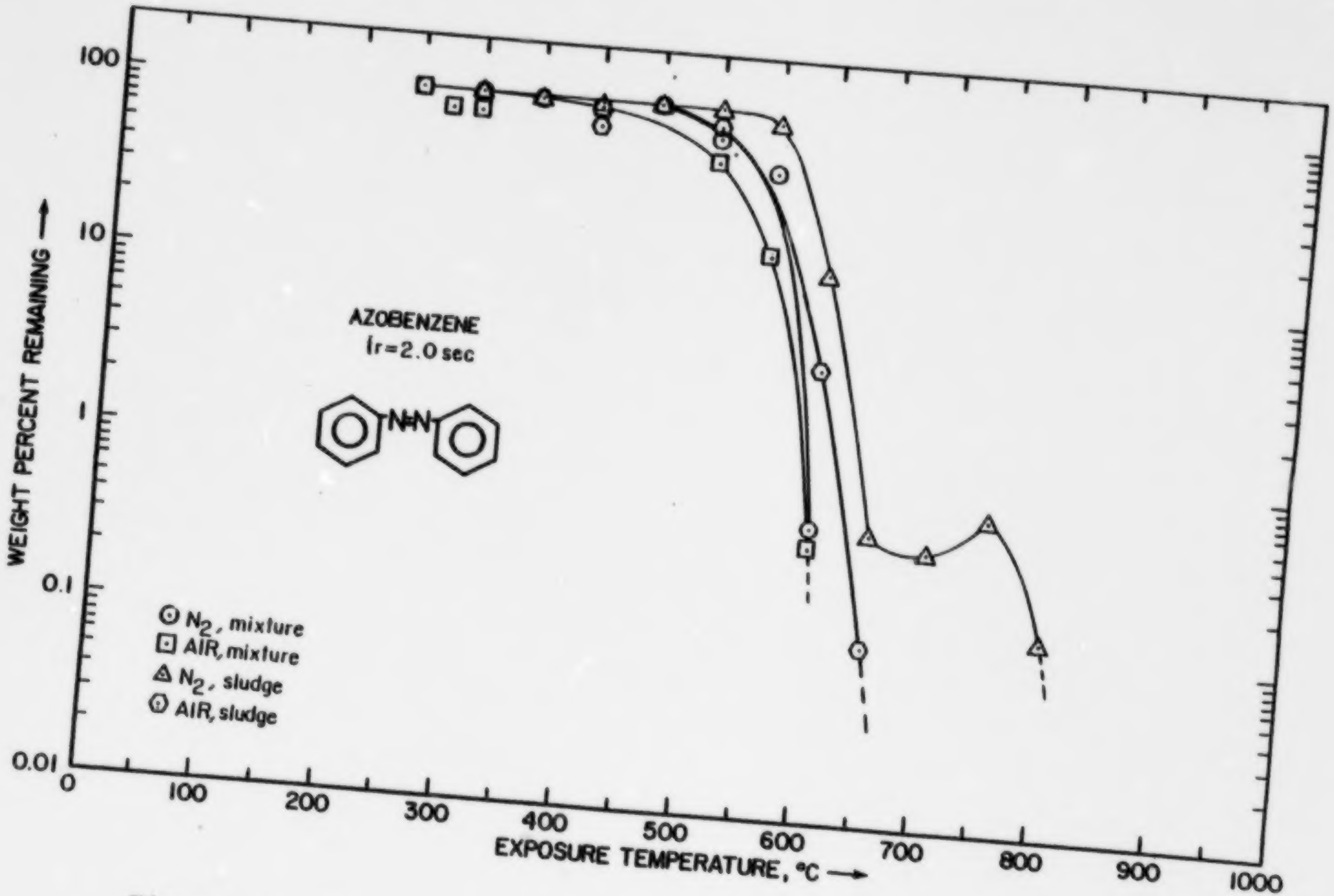


Figure 15. Thermal decomposition profiles for azobenzene.

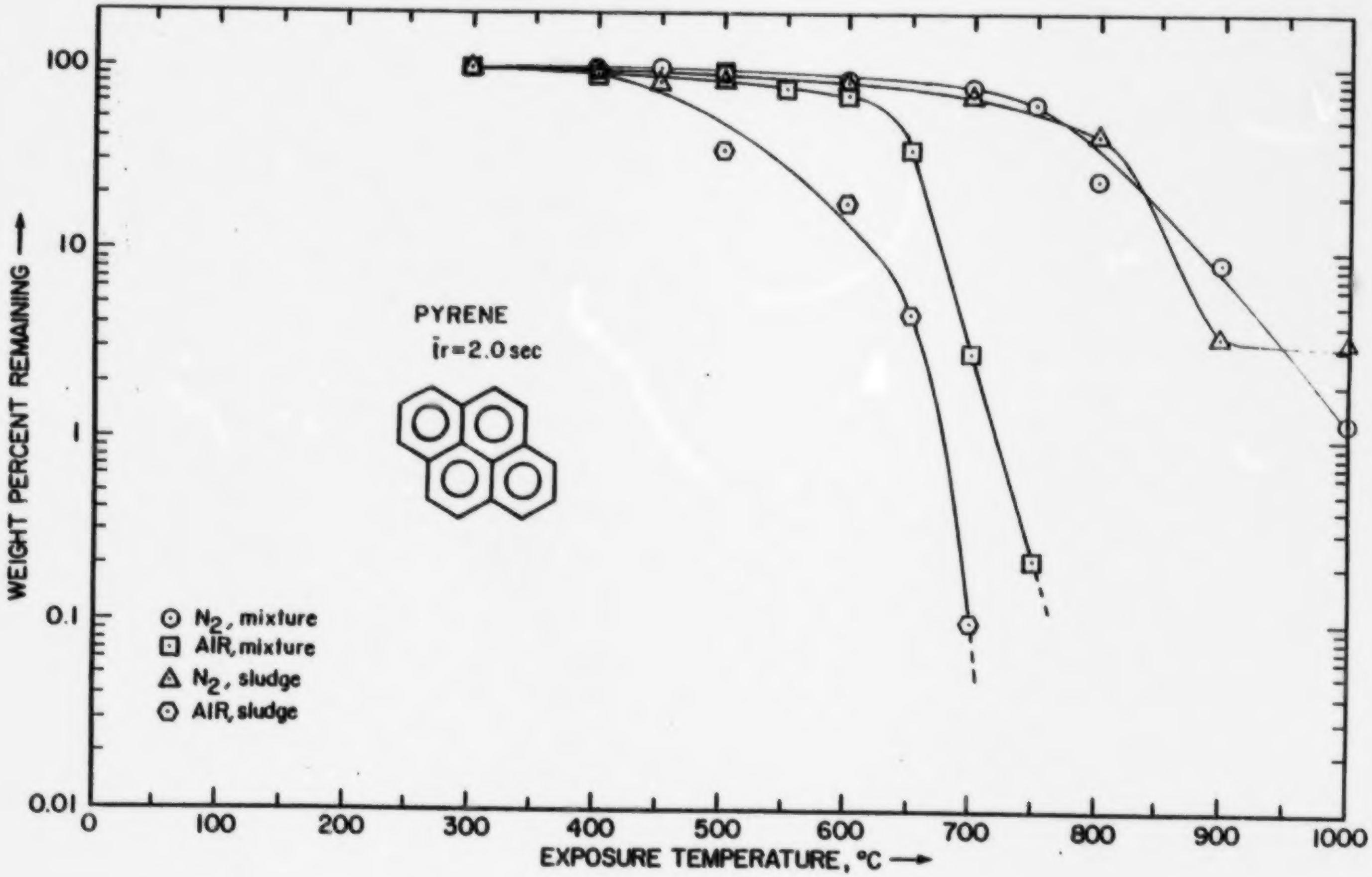


Figure 16. Thermal decomposition profiles for pyrene.

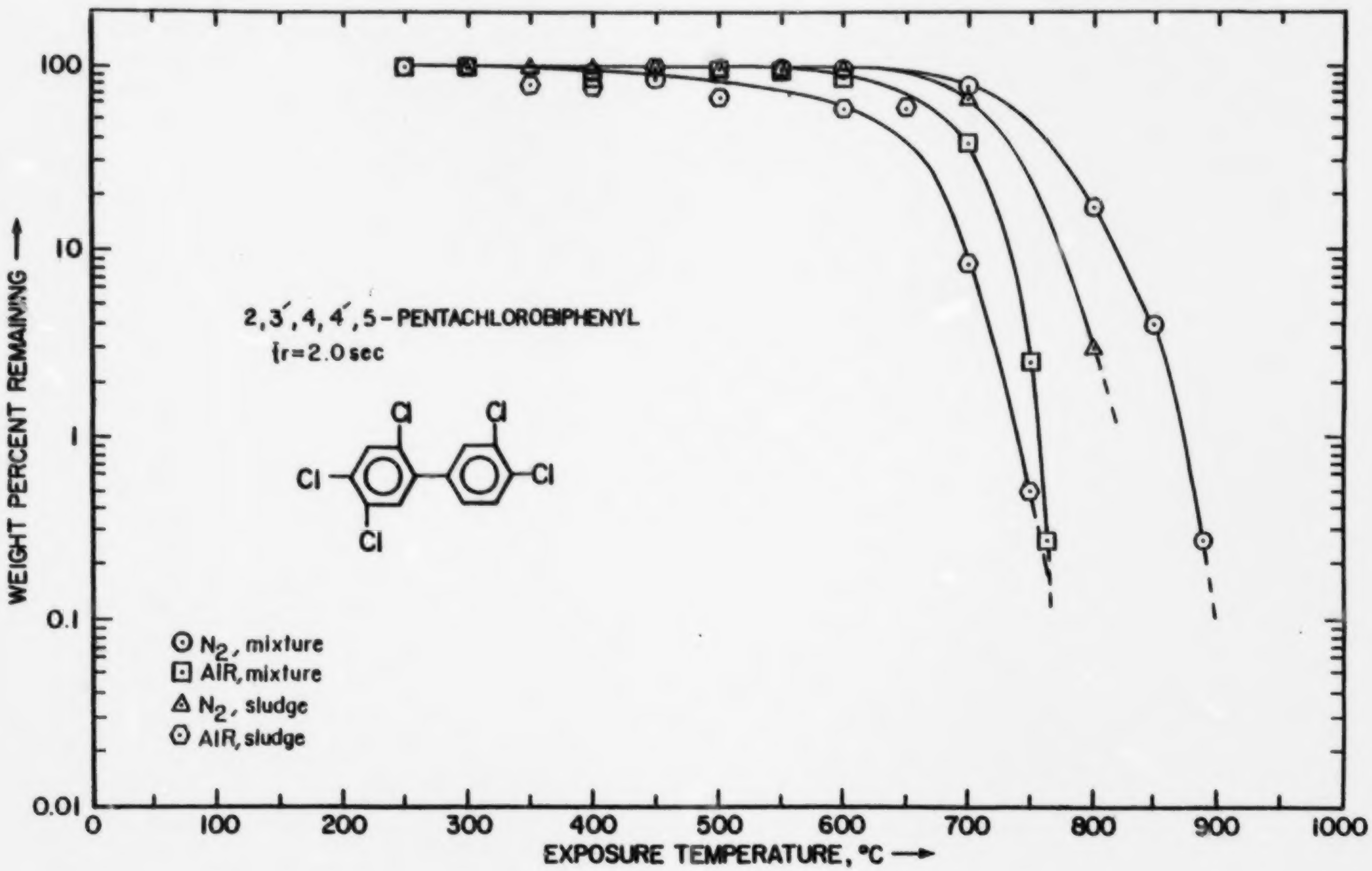


Figure 17. Thermal decomposition profiles for 2,3',4,4',5-pentachlorobiphenyl.

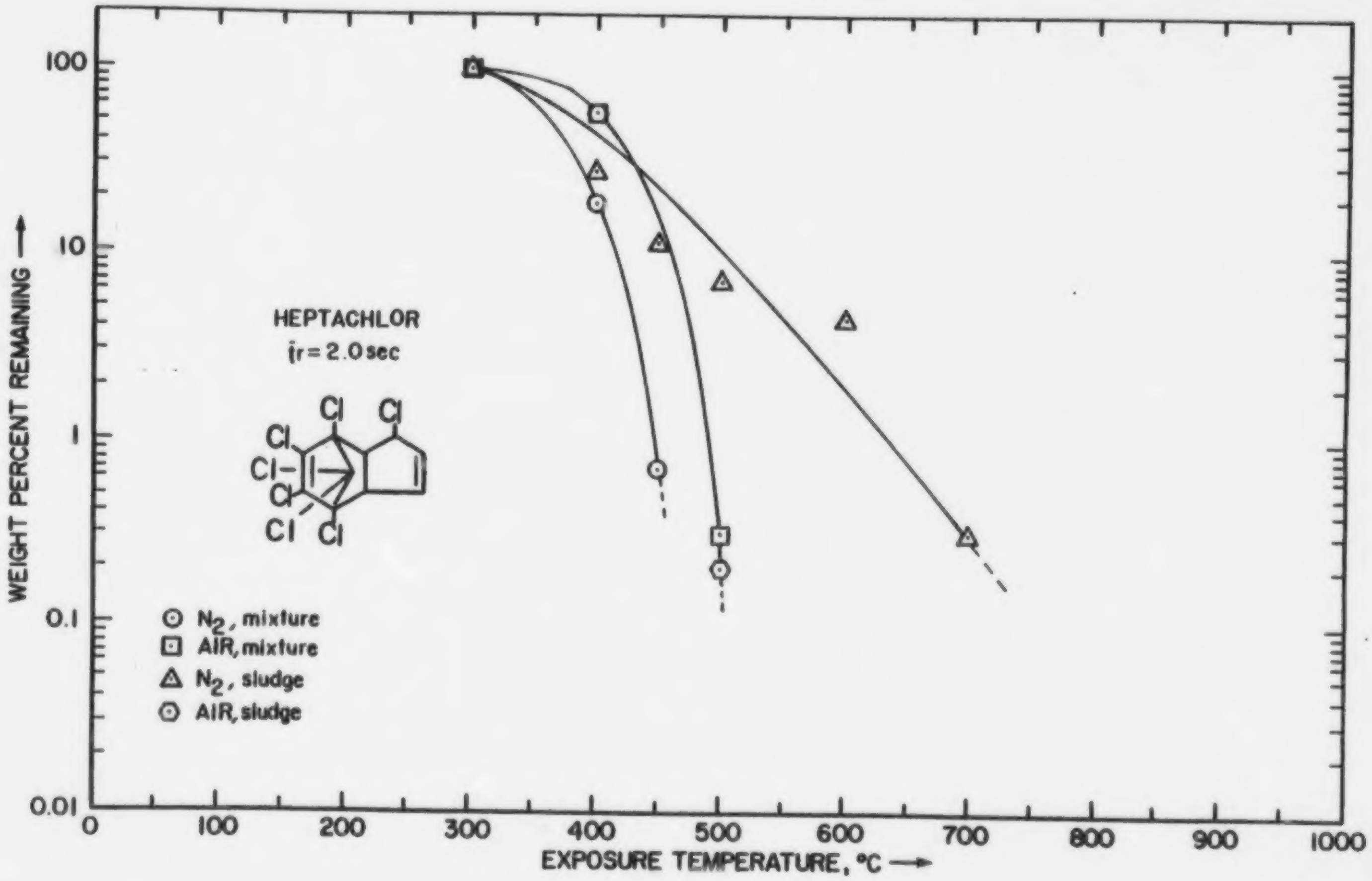


Figure 18. Thermal decomposition profiles for heptachlor.

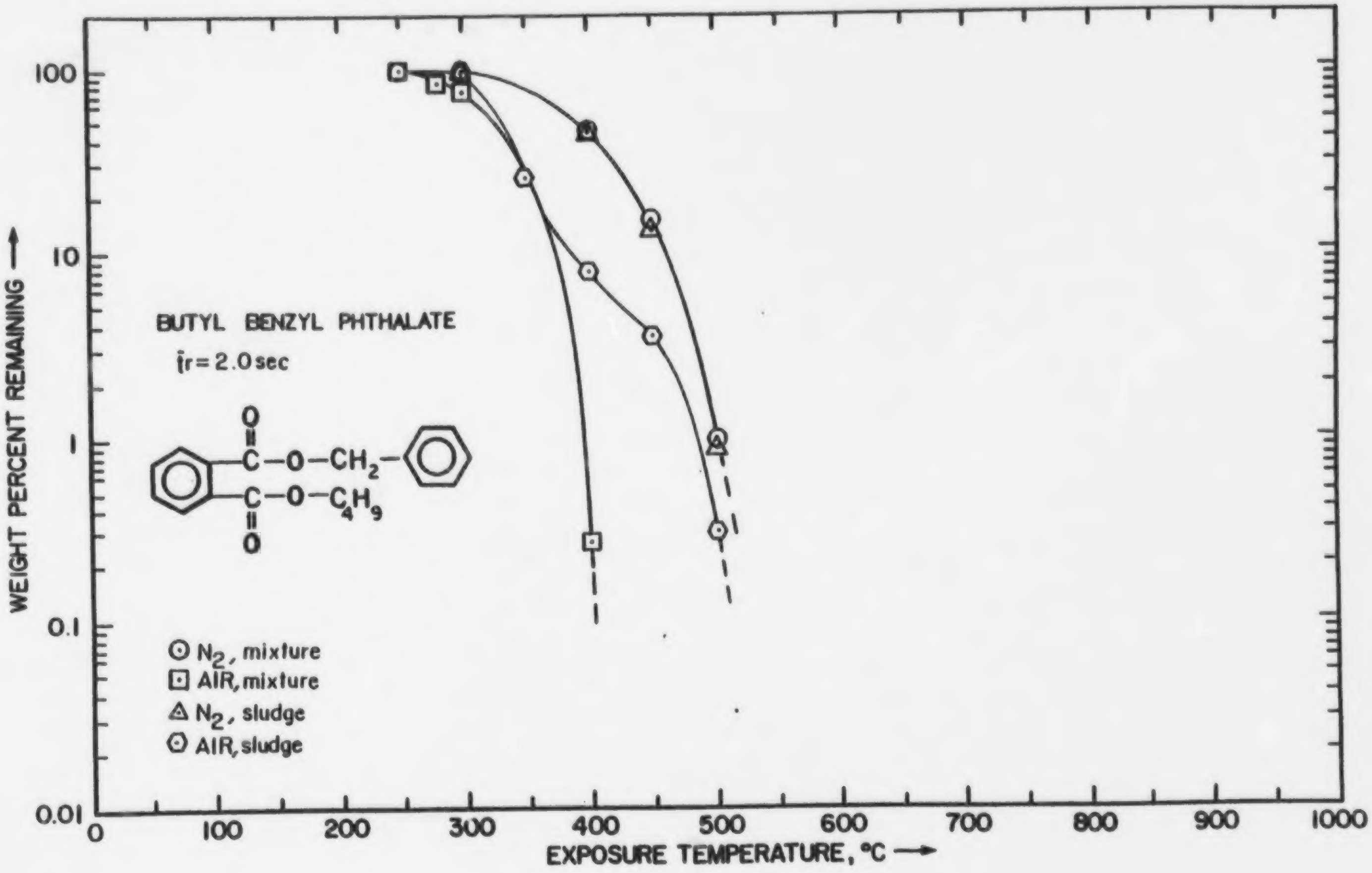


Figure 19. Thermal Decomposition Profiles for butyl benzyl phthalate.

TABLE 8. EFFECT OF SAMPLE MATRIX ON THERMAL STABILITY OF COMMON SLUDGE CONTAMINANTS

Spike Compound	Stability In Nitrogen Atmoxphere	Possible Reason[a]	Stability In Air Atmosphere	Possible Reason[a]
Diphenylamine	Sludge>Mixture	Scavenging	Sludge >Mixture	Scavenging
Nonylphenol	Sludge>Mixture	Scavenging	Sludge >Mixture	Scavenging
Pentachlorophenol	Sludge>Mixture	Interference (high temperature) + Scavenging (low temperature)	Sludge >Mixture	Scavenging
Azobenzene	Sludge>Mixture	Scavenging (low temperature) + PIC (high temperature)	Sludge >Mixture	Scavenging
Pyrene	Sludge>Mixture	PIC	Mixture>Sludge	Radicals from Sludge
2,3',4,4',5-Pentachlorophenol	Mixture >Sludge	Radicals from Sludge	Mixture>Sludge	Radicals from Sludge
Heptachlor	Sludge >Mixture	Interference	Sludge=Mixture	Unimolecular Decomposition
Butyl benzyl phthalate	Sludge=Mixture	Unimolecular Decomposition	Sludge >Mixture	Interference

---

[a] Possible Reasons (see text for greater details):

- Scavenging = sludge scavenges reactive radicals needed to initiate decomposition of contaminants.
- PIC = contaminant formed as PIC from sludge, thereby causing contaminant to appear more stable.
- Interference = coeluting sludge component causes contaminant to appear more stable.
- Radicals from Sludge = sludge produces radicals which initiate decomposition of contaminants.
- Unimolecular Decomposition = contaminant decomposes unimolecularly; hence, matrix has no effect.

greater than that produced by the chemical noise of the sludge. It can be concluded that chromatographic interferences are not the major cause for the apparent greater thermal stability of POHCs in sludge.

The second possible explanation for the matrix phenomenon is that a POHC is being formed as a PIC from the decomposition of the sludge. This is the probable explanation for the "hump" in the azobenzene curve between 700°C and 800°C in the spiked sludge in nitrogen. Diphenylamine could also possibly form as a PIC from sludge, although there are no irregularities in the decomposition curves to indicate that this is happening. Pentachlorophenol and nonylphenol are not at all likely to be formed as PICs from sludge.

The most likely explanation in most cases for the greater apparent stability of these compounds in sludge is that the sludge scavenges the radicals necessary to initiate the thermal decomposition of the POHCs. The fact that all these compounds decompose in a moderate temperature range, where much of the sludge matrix remains undecomposed, lends credence to this idea. Whether the radical scavenging effect of the sludge is a bulk effect or whether it can be attributed to select components is as yet unknown.

For two of the POHCs tested under this program, the sludge had the opposite effect on thermal stability. For a given atmosphere, pyrene and the PCB were actually more fragile in the sludge matrix. (An apparent exception to this is the pyrene curve for the spiked sludge in nitrogen, where the curve crosses over the mixture curve between 900°C and 1000°C. The irregular shape of this curve, along with the observation that many PNAs were produced as PICs from sludge, leads one to conclude that pyrene is being formed as a PIC from sludge, and that if it were not for PIC formation, pyrene would be more fragile in sludge throughout the temperature range.)

It is interesting to note that the compounds which were less stable in the sludge were the two which decomposed at higher temperatures in the mixtures. These relatively stable compounds persist to high temperatures where much of the sludge matrix is already destroyed and that which remains is rapidly decomposing. In this temperature range, the sludge is producing radicals which can then attack the POHCs, and this may be responsible for their enhanced thermal decomposition.

Thermal decomposition of the remaining two POHCs - heptachlor and butyl benzyl phthalate - shows little if any dependence on the sludge. For both these compounds, the curves in one atmosphere lie directly on top of one another. In the other atmosphere, it is suspected that an interference is causing the compound to appear more stable in the sludge. For heptachlor, the mass spectral data confirm this hypothesis. For butyl benzyl phthalate, confirming mass spectral data have not been obtained. However, the fact that the phthalate decomposes in a temperature range where most of the sludge remains undecomposed, along with the fact that the curves in nitrogen diverge when less than 10% of the phthalate remains, certainly makes an interference seem plausible. The unusual shape of the curve further supports this hypothesis.

Both heptachlor and butyl benzyl phthalate are very fragile compounds, and it may be postulated that they undergo unimolecular decomposition. Concerted elimination of HCl may constitute a low-energy decomposition pathway for heptachlor. It is likely that if analytical interferences were removed, all curves for this compound would show virtually identical temperature dependence. Butyl benzyl phthalate may decompose by an internal cyclization reaction wherein an alkyl hydrogen attacks the carbonyl oxygen and a six-membered ring is formed [36]. This mechanism may predominate in the nitrogen atmosphere. The compound is more fragile in air than in nitrogen, so OH abstraction of the benzylic hydrogen may initiate the decomposition in air.

In sum, then, the sludge exerted mixed effects on the ease with which the common hazardous contaminants (POHCs) could be destroyed. Based on the limited data base of eight POHCs, the following trends were observed:

- The sludge exerted little if any effect on the ease of destruction of very fragile POHCs.
- If a POHC was intermediate in thermal stability, it was more difficult to destroy in the presence of the sludge.
- If a POHC was very stable in the pure mixture, the sludge enhanced its ease of destruction.

Products of Incomplete Combustion from Common Sludge Contaminants

It is fortunate that common sludge contaminants, such as butyl benzyl phthalate, heptachlor and nonylphenol are readily thermally destroyed relative to the bulk of the other hazardous compounds tested in our laboratory. It is unfortunate, however, that these compounds decompose to form PICs which are more difficult to incinerate. These PICs are discussed below.

Major thermal decomposition products for spiked sludges, spiking solutions, and unspiked sludge are given in Tables C.1 through C.7 of Appendix C. The specific data presented in each table are given below:

Table C.1. Composite A Spiked Sludge
Table C.2. Composite A Spike Solution
Table C.3. Composite B Spiked Sludge
Table C.4. Composite B Spike Solution
Table C.5. Nonylphenol Spiked Sludge
Table C.6. Nonylphenol Spike Solution
Table C.7. Unspiked Sludge

For the Composite A and Composite B spiked sludges and spike solutions, an attempt was made to segregate the PICs based on their probable POHC precursors. In doing this, structural similarity and presence or absence of heteroatoms were the primary criteria for assigning PICs to particular parents. For example, the chlorinated PICs from the Composite A studies were assigned to either heptachlor or pentachlorophenol (PCP), while nitrogen-containing PICs were attributed to the nitrosamine parent.

Results of the above-described data analysis are given in Figures 20 through 27. Some PICs were not assigned to a particular parent because they were likely products from the sludge (e.g., alkenes, benzene, styrene, toluene), and/or because they may have been formed from any of the starting materials (e.g., benzene).

PICs were relatively easily assigned for the four POHCs present in the Composite A mixture. The only difficulty was the chlorinated PICs, which could have been assigned to either heptachlor or PCP. Results from the pure PCP decomposition were used to guide the assignment. If a given PIC was detected as a decomposition product from pure PCP, it was assigned to that parent, if not, it was assigned to heptachlor. This approach is arbitrary in that a given PIC could have both POHCs as precursors, and in that PCP decomposition may yield different PICs depending upon whether the compound is run in a pure form, in a mixture, or on sludge.

PICs from the Composite B samples were not as readily assigned. A number of oxygen-containing PICs could be attributed to the butyl benzyl phthalate parent, but only one PIC could be attributed clearly to the azobenzene, and no unique PICs were found for the PCB. The Composite B mixture yielded PICs such as benzene, toluene, and styrene which could have been formed from any of the starting materials and hence remained unassigned.

A recent study of the 2,3',4,4',5-pentachlorobiphenyl isomer as a pure compound showed that chlorinated aromatics such as dibenzofurans, benzenes, naphthalenes, and lower chlorinated biphenyls were formed as thermal reaction products [25]. It may be that in the present study, the PCB yielded a

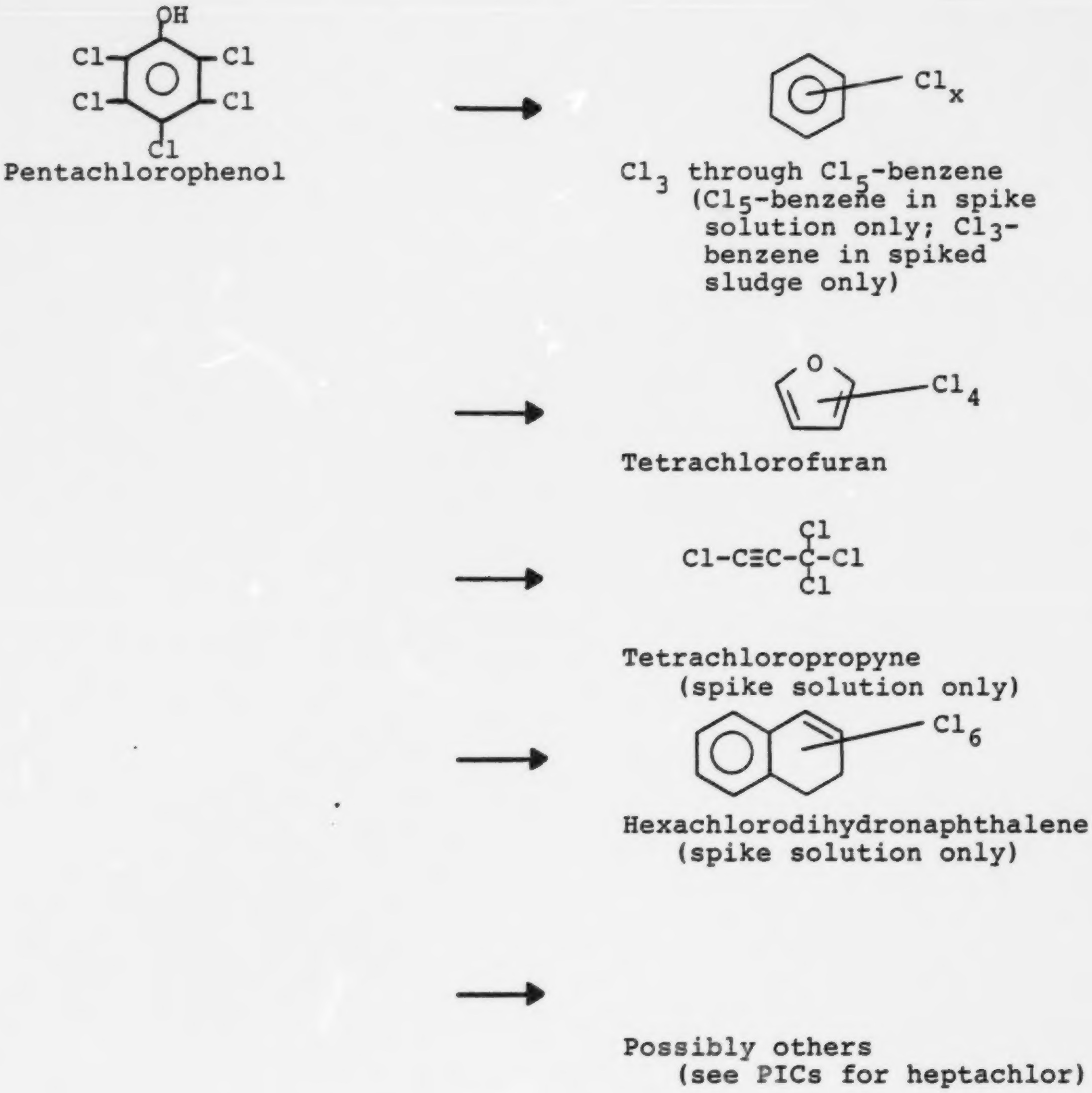

OH
Cl
Cl
Cl
Cl
Cl
Pentachlorophenol
Cl$_x$
Cl$_3$ through Cl$_5$-benzene (Cl$_5$-benzene in spike solution only; Cl$_3$-benzene in spiked sludge only)
O
Cl$_4$
Tetrachlorofuran
Cl-C≡C-C(Cl)$_2$-Cl
Tetrachloropropyne (spike solution only)
Cl$_6$
Hexachlorodihydronaphthalene (spike solution only)
Possibly others (see PICs for heptachlor)

Figure 20. PICs attributed to pentachlorophenol.

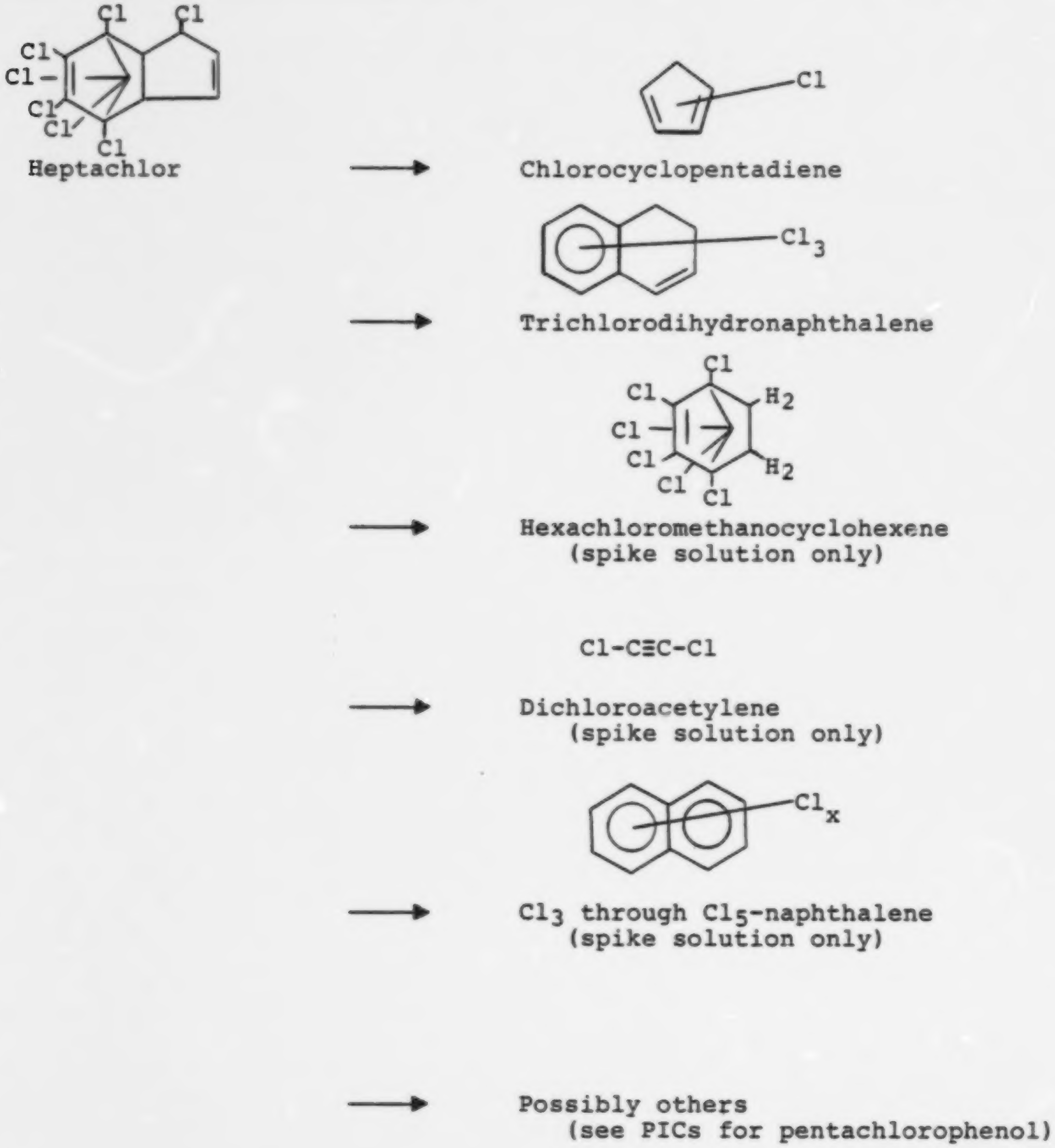

Cl
Cl
Cl
Cl –
Cl
Cl
Cl
Heptachlor
Cl
Chlorocyclopentadiene
Cl3
Trichlorodihydronaphthalene
Cl
Cl
Cl –
Cl
Cl
Cl
H2
H2
Hexachloromethanocyclohexene
(spike solution only)
Cl-C≡C-Cl
Dichloroacetylene
(spike solution only)
Clx
Cl3 through Cl5-naphthalene
(spike solution only)
Possibly others
(see PICs for pentachlorophenol)

Figure 21. PICs attributed to heptachlor.

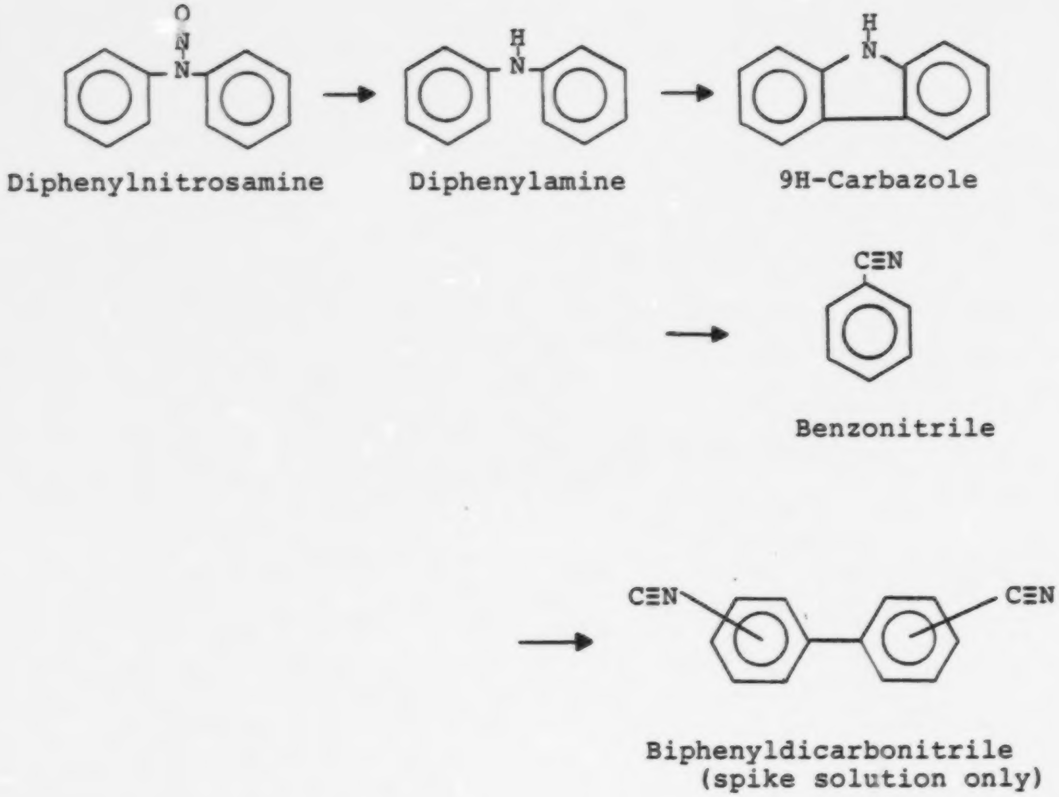

O
N
N
H
N
H
N
Diphenylnitrosamine
Diphenylamine
9H-Carbazole
C≡N
Benzonitrile
C≡N
C≡N
Biphenyldicarbonitrile
(spike solution only)

Figure 22. PICs attributed to diphenylnitrosamine.

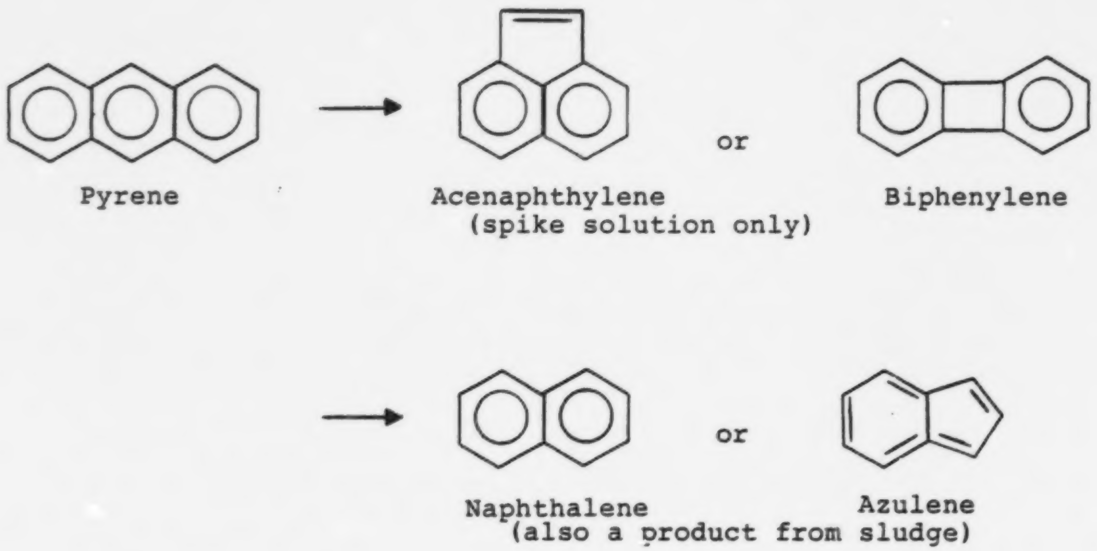

Pyrene
Acenaphthylene
(spike solution only)
or
Biphenylene
Naphthalene
(also a product from sludge)
or
Azulene

Figure 23. PICs attributed to pyrene.

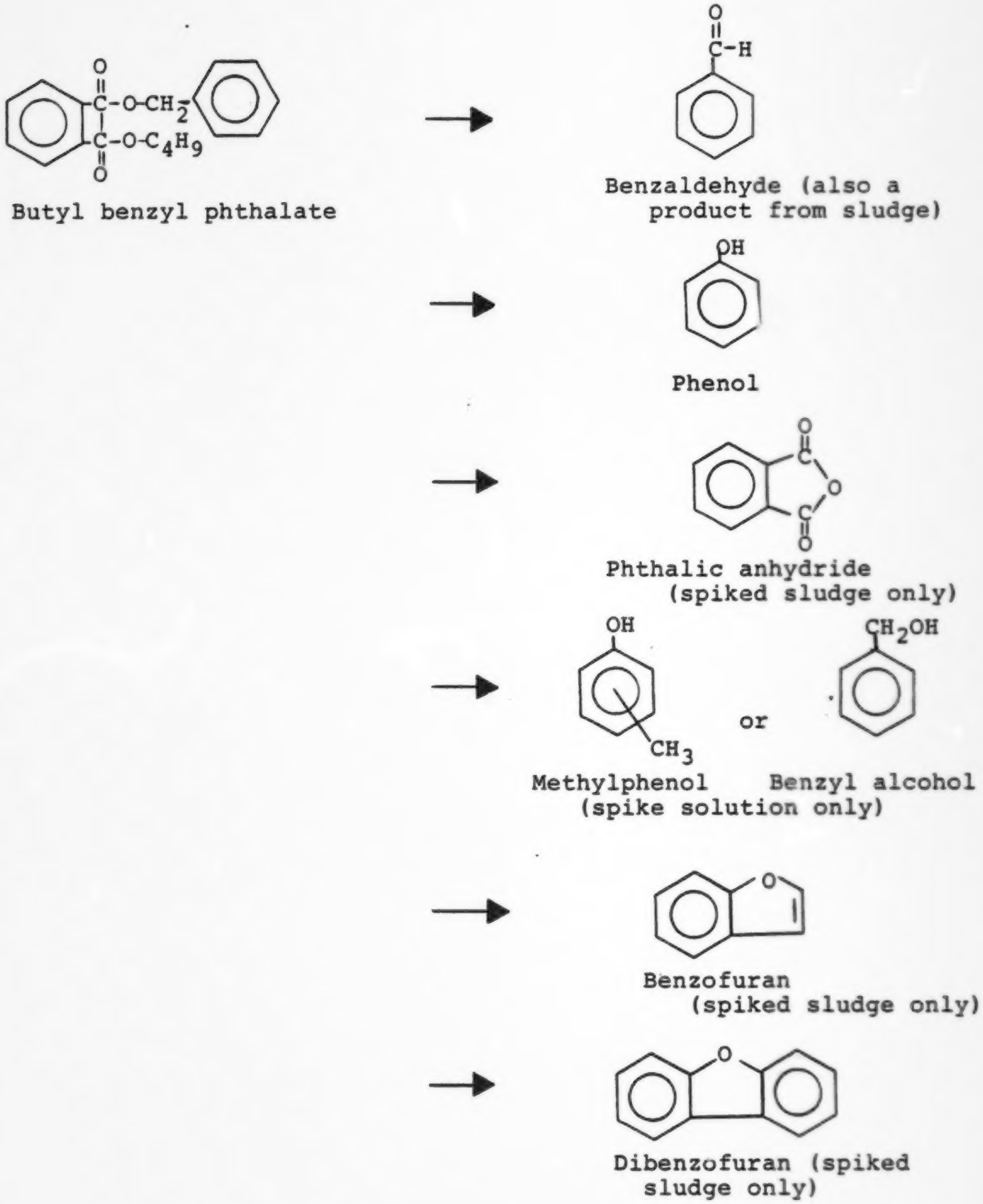
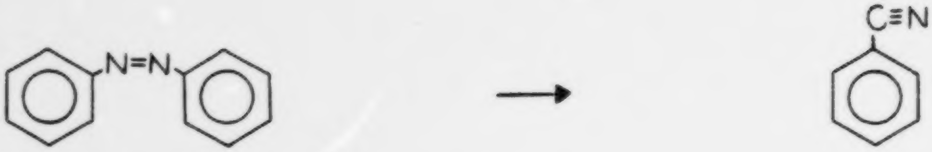

Butyl benzyl phthalate
Benzaldehyde (also a product from sludge)
Phenol
Phthalic anhydride (spiked sludge only)
Methylphenol
or
Benzyl alcohol
(spike solution only)
Benzofuran (spiked sludge only)
Dibenzofuran (spiked sludge only)

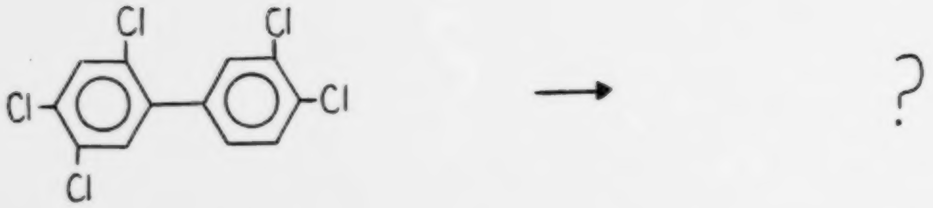
Figure 24. PICs attributed to butyl benzyl phthalate.



Azobenzene

Benzonitrile
(spiked sludge only)

Figure 25. PICs attributed to azobenzene.



2,3',4,4',5-Pentachlorobiphenyl

Figure 26. PICs attributed to 2,3',4,4',5-Pentachlorobiphenyl.

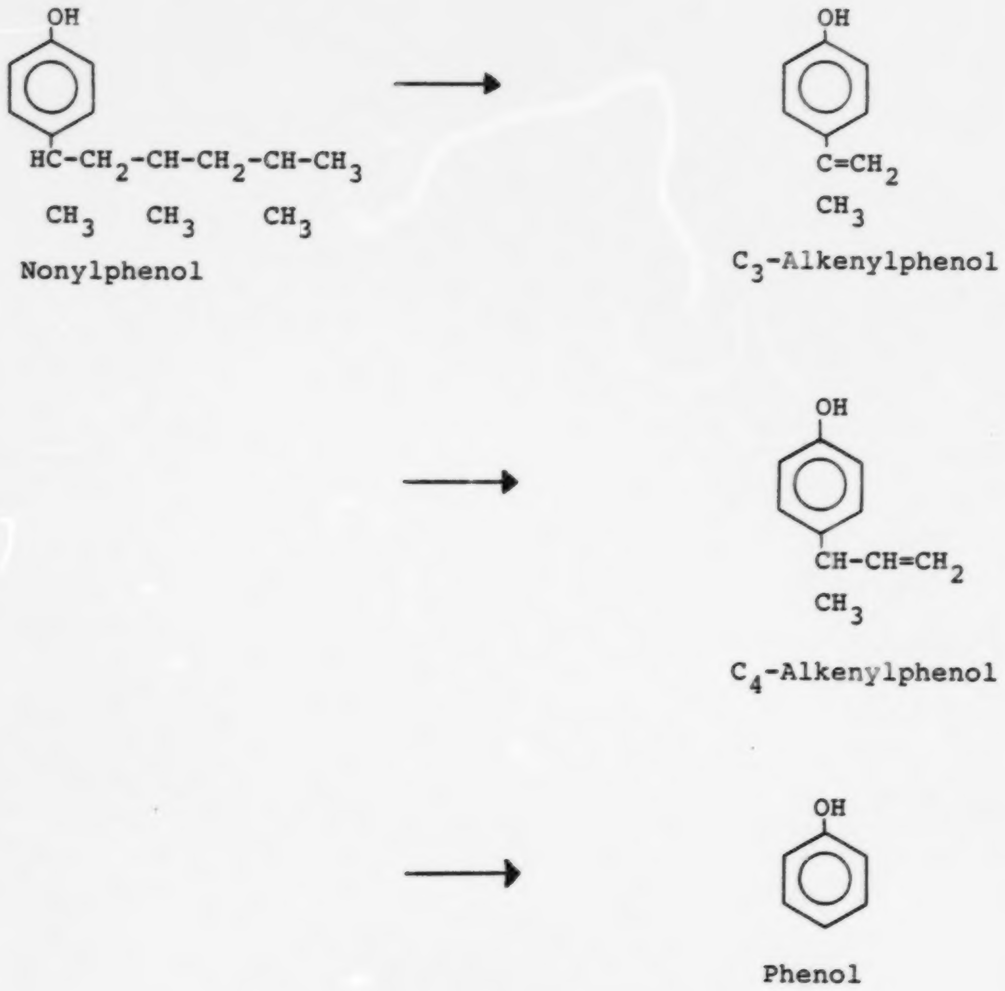

OH
HC-CH2-CH-CH2-CH-CH3
CH3 CH3 CH3
Nonylphenol
OH
C=CH2
CH3
C3-Alkenylphenol
OH
CH-CH=CH2
CH3
C4-Alkenylphenol
OH
Phenol

Figure 27. Major PICs from nonylphenol.

multitude of products, but that the individual yields were below detection limits.

The highest-yield thermal reaction products from the nonylphenol-spiked sludge are shown in Figure 27. As Tables C.5 and C.6 indicate, many additional PICs were formed in lower yields.

So that a preliminary indication could be obtained on the importance of the specific sludge in the thermal decomposition of a sludge contaminant, nonylphenol decomposition was studied on two different sludges. These sludges were obtained on different days from the same wastewater treatment plant, and were the products of slightly different processing. When decomposed under identical conditions, these two spiked sludges yielded an identical set of major PICs, but the relative PIC yields differed. While changing the sludge did not appear to exert a great influence on the results in this case, more dramatic effects may be obtained by testing more dissimilar sludges and more sensitive contaminants.

Table C.7, which lists products from the unspiked sludge, indicates that aromatic compounds such as benzene, toluene, styrene, benzaldehyde, ethylbenzene/xylene, and naphthalene/azulene were formed as decomposition products from the sludge. Benzene and styrene have produced tumorigenic, mutagenic, reproductive, and toxic effects in animal tests. Benzene is a known human carcinogen and styrene is a known animal carcinogen and a suspected human carcinogen. It should be noted that the particular sludge tested here originated in a nonindustrialized municipality. The conclusion to be drawn here is that improper incineration of even relatively uncontaminated sludge may result in production of PICs which are on EPA's Appendix VIII list and which may have adverse human health effects.

In Figures 20 through 27, a note was made whenever a given PIC was present for only the spiked sludge or the spiking solution, rather than both. This suggests that the sample matrix was changing the PICs that were produced. This hypothesis is only tentative based on the data presented thus far, because in most cases the spiked sludge and spiking composites were not run under an identical set of reactor temperatures.

More definite conclusions can be reached concerning the effect of the sludge if PICs from the two matrices are compared under identical experimental conditions. This type of comparison clearly shows that the presence of the sludge changed the number and types of PICs which were produced under a given reactor temperature and atmosphere. This can be observed by comparing, for example, the Composite A results for the spiked sludge (Table C.1) versus the spike solution (Table C.2). The experimental conditions which overlap for the two sets of conditions are the 500°C runs in nitrogen and air, the 650°C run in air, and the 800°C run in nitrogen. These data have been reformatted as Table C.8 so that the effect of the sludge can be more readily observed. This reformatted table shows that there were nine cases where a given PIC was detected under a given set of conditions as a major product in both the spiked sludge and the spiking solution. However, there were 24 cases where a PIC was detected under a given set of conditions in either the spiked sludge or the spike solution, but not both. Furthermore, there were two cases where a PIC derived from the spike materials constituted one of the highest yield products in one matrix, but was not even detected as a major product in the other matrix. One may conclude that at a given temperature and oxygen level, the presence of the sludge altered the decomposition mechanism for the sludge contaminants.

During the early stages of this research, the sludge samples were introduced into the TDU-GC and TDAS using a slightly different procedure in which the insertion region was heated 100°C higher than in the standard procedure. This technique was later abandoned because some organics (and possibly metals) which volatilized from the sludge were too heavy to be quantitatively transported through the system; these visibly contaminated the quartz flowpath, producing potentially adsorptive and catalytic sites. Prior to the discovery and clean-up of this contamination, some rather interesting data were obtained for the Composite A spiked sludge in the nitrogen atmosphere. These data are presented in Tables C.9 through C.11.

There were some interesting differences in the data obtained under these conditions versus the standard conditions. First of all, the TDU-GC chromatograms showed that additional high molecular weight species were desorbed from the sludge when the insertion region was hotter. TDAS data indicated that these were primarily compounds having the cholesterol fused-ring system as part of their structure. TDAS data also indicated that additional PICs were formed at higher reactor temperatures. The additional PICs were primarily polynuclear aromatics (PNAs), chlorinated PNAs, and alkenes. Comparison of Table C.1 with Tables C.9 and C.10 shows that the following additional PICs were present when the insertion region temperature was raised:

500°C, N_2	800°C, N_2
Cholest-ene (10 isomers)	Pentachlorobenzene
Cholest-ene-dione or cholest-dien-ol (3 isomers)	Trichloronaphthalene (3 isomers)
Epoxy cholestane	Tetrachloronaphthalene

Phthalic anhydride
C_{14}-alkene or cycloalkane
C_{15}-alkene or cycloalkane
C_{16}-alkene or cycloalkene (2 isomers)
C_{17}-alkene or cycloalkene
C_{19}-alkene or cycloalkane (2 isomers)
Dodecylbenzene
Fluoranthene

Pentachloronaphthalene
Methylnaphthalene (2 isomers)
Acenaphthylene or biphenylene
Diphenylamine

Anthracene or phenanthrene
Aromatic compound with possible formula $C_{15}H_{10}$
Trichlorobenzene (2 isomers)
Quinoline or isoquinoline
Acenaphthylene or biphenylene
Biphenyl
Naphthalene carbonitrile (2 isomers)
9-H-Fluorene or isomer (2 peaks)
Tetrachlorostyrene
Anthracene or phenanthrene (second peak)
Tetrachlorodihydronaphthalene
Biphenyl dicarbonitrile
Pentachloronaphthalene

These lists suggest that the cholesterol-like compounds present in sludge (from bile salts, natural and synthetic hormones, and cell membranes) may contribute to PNA emissions. Many PNAs are on the Appendix VIII list of hazardous compounds.

Data from Tables C.9 through C.11 are summarized in Figure 28, which shows the relative types and concentrations of PICs from the Composite A spiked sludge (high insertion region temperature) versus the spiking solution. This graph shows that much higher levels of PICs were formed from the spiked sludge than from the spiking mixture, which indicates that the majority of the PICs were formed from the biomass. This is not surprising since even at the relatively high spike levels that were used, the total weight of organic material associated with the biomass was about 1000 times that of the spikes.

Figure 28 also shows the predominant classes of PICs produced at each of three reactor temperatures. The graph indicates that for the spiked sludge, the bulk of the thermal reaction products at 500°C were cholesterol-like compounds, while at 800°C PNAs and chlorinated hydrocarbons predominated, and at 1000°C only PNAs remained. Based on these data, as well as data from the thermal decomposition of unspiked sludge (Table C.7), the major high-temperature emissions from a sewage sludge incinerator would be expected to be PNAs and aromatics such as benzene, styrene, toluene, etc. Chlorinated PNA emissions could possibly be significant at industrialized sites.

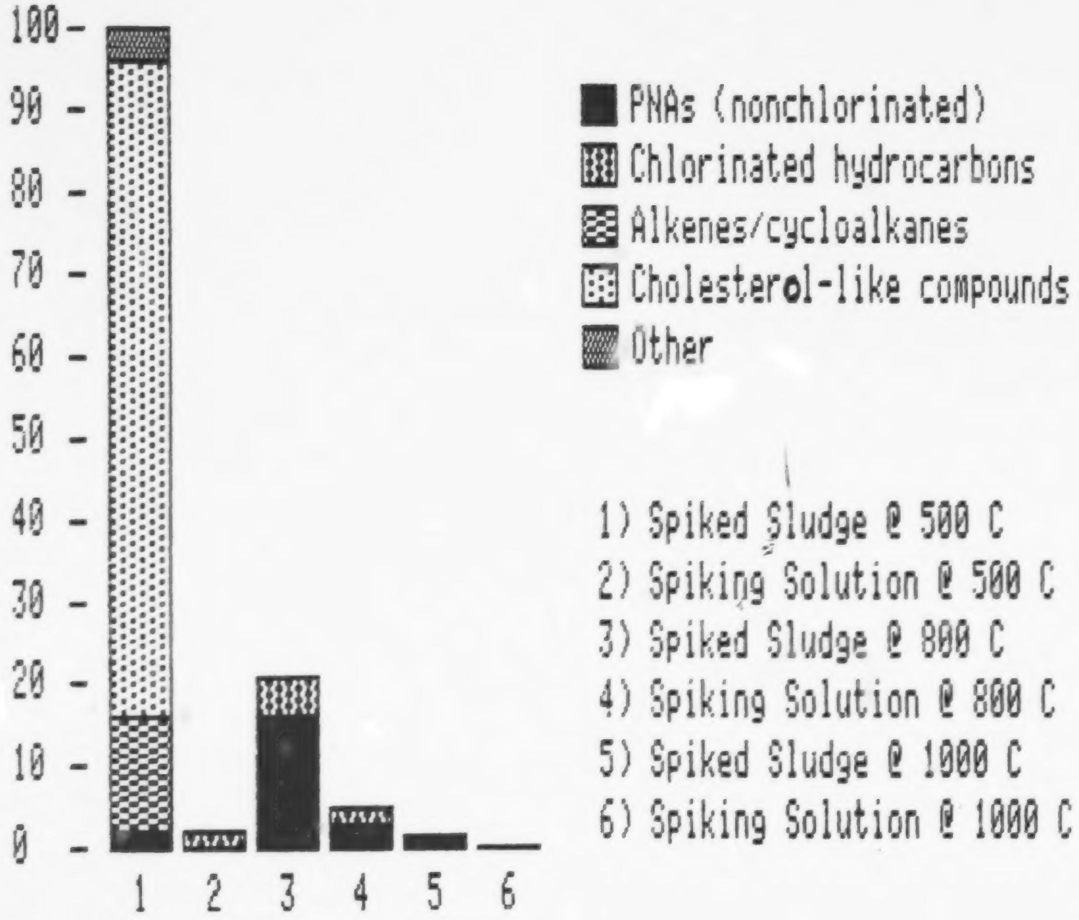


Figure 28. Relative quantities of various classes of PICs resulting from thermal decomposition of composite A spiked sludge and spiking solution at three reactor temperatures.

THERMAL DECOMPOSITION OF RELATED PURE COMPOUNDS

To gain a better understanding of the spiked sludge data, the thermal decomposition of pentachlorophenol was studied in both air and nitrogen atmospheres. The resulting thermal decomposition profiles are shown in Figure 29. Temperatures for 99.9% decomposition were 630°C in air and 640°C in nitrogen. Very little oxygen dependence was observed, which at first suggested that the decomposition may be unimolecular. However, later studies with pentachlorophenol in a mixture, as well as in the spiked sludge, showed that the decomposition rate of the PCP was highly matrix dependent. For example, Figure 14 showed that in the mixture, temperatures for 99.9% decomposition were about 720°C in air and 760°C in nitrogen, about 100°C higher than with the pure compound. Still greater temperatures were required for 99.9% destruction when sludge was present. This matrix dependence is inconsistent with a unimolecular decomposition mechanism.

Major products of incomplete combustion were identified for PCP in nitrogen and in air using the TDAS. These partial combustion products, along with their temperature of maximum formation, are given in Table 9. From profiling the combustion products, it was observed that all were formed at approximately equal concentrations (within a factor of 10), at their temperatures of maximum yield. Figure 30 depicts the formation and destruction profile for octachloronaphthalene, which was the highest yield product in nitrogen, while Figure 31 shows a similar profile for tetrachloroethylene, the product of highest yield in air.

It was observed that the formation maxima for PICs generally peaked about 630 to 650°C for pentachlorophenol in air and 725 to 775°C for pentachlorophenol in nitrogen. This is interesting in light of the fact that the parent material exhibited a maximum decomposition rate between 625°C and 650°C in both cases. This may have occurred because in air PICs were forming directly from the parent material, while in nitrogen, the principal PICs may have evolved through thermal decomposition of other PICs.

It is noteworthy that none of the major PICs from PCP retain the OH moiety, and that none of the major PICs in nitrogen retain the oxygen. Also, as a class, chlorinated benzenes seem to be the most prevalent PICs.

It is possible that in nitrogen, H attack on the hydroxyl functionality, followed by loss of water, constitutes a significant decomposition pathway. Water loss may occur in the air atmosphere as well, although the exact mechanism is uncertain. Also, in the air atmosphere, chlorinated furans are formed as PICs. It is not clear whether the oxygen in these

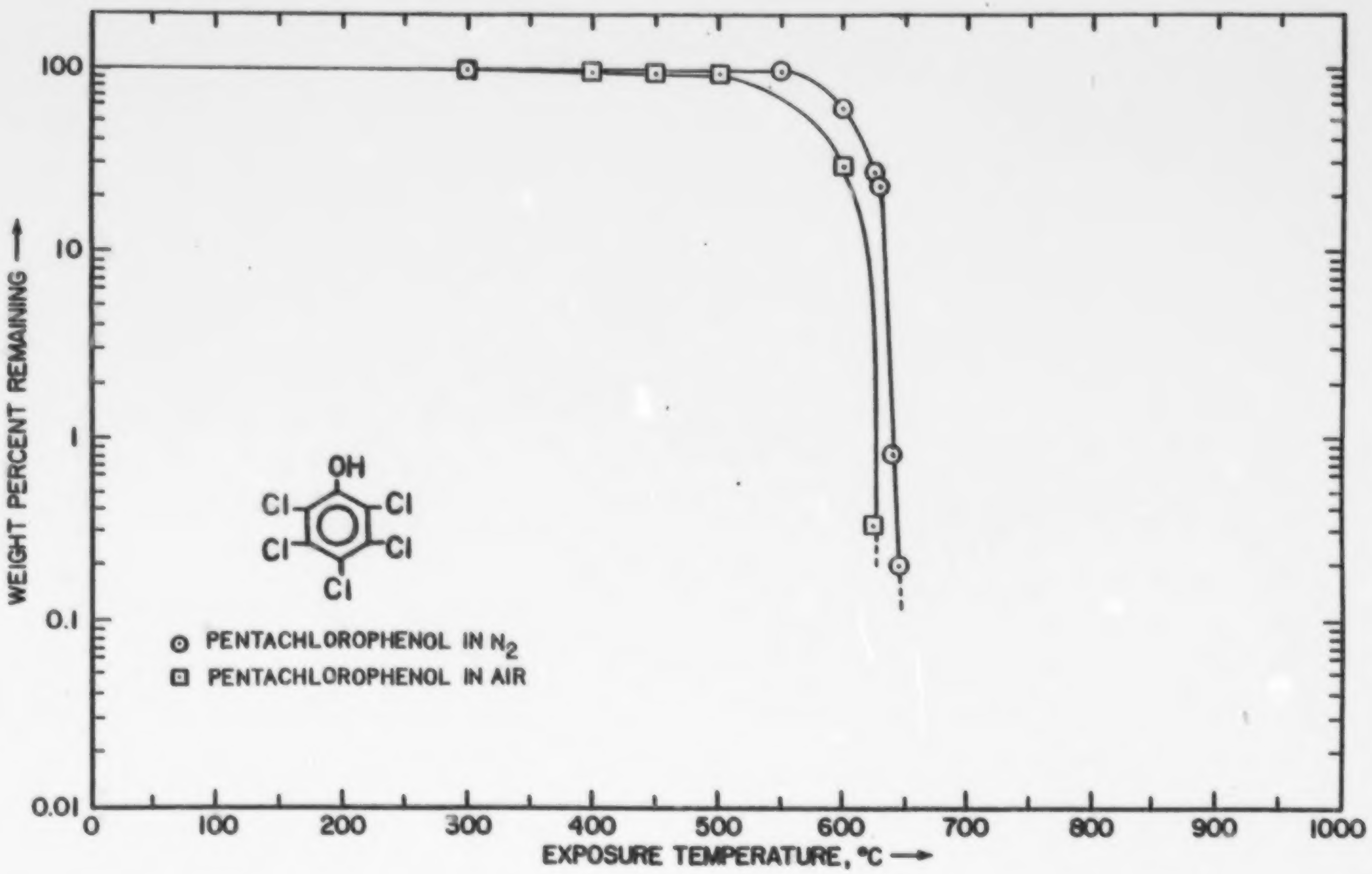


Figure 29. Thermal decomposition profiles for pentachlorophenol.

TABLE 9. THERMAL DEGRADATION PRODUCTS FROM PENTACHLOROPHENOL[a]

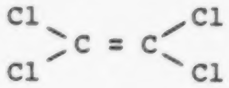
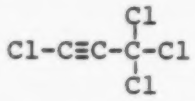
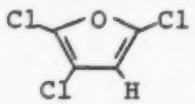
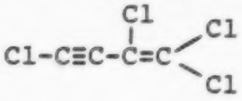
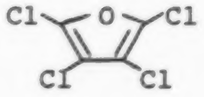
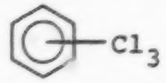
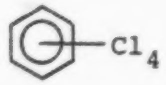
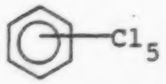
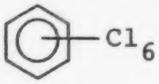
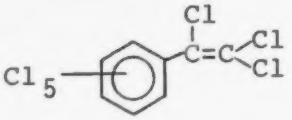
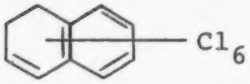
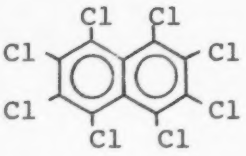
Tentative Identification	Tentative Structure	Temperature of Maximum Formation (C)	
		In N_2	In Air
Dichlorobutadiyne	$\mathrm{Cl{-}C{\equiv}C{-}C{\equiv}C{-}Cl}$	800	ND[b]
Tetrachloroethylene	 $\mathrm{Cl_2C=CCl_2}$	ND	650
Tetrachloropropyne	 $\mathrm{Cl{-}C{\equiv}C{-}CCl_3}$	ND	630
Trichlorofuran		ND	630
1,1,2,4-tetrachloro-1-buten-3-yne	 $\mathrm{Cl{-}C{\equiv}C{-}C(Cl){=}CCl_2}$	725	630
Tetrachlorofuran		ND	650
Trichlorobenzene		625	630
Tetrachlorobenzene		775	630
Pentachlorobenzene		725	630

TABLE 9. THERMAL DEGRADATION PRODUCTS FROM PENTACHLOROPHENOL[a] (CONTINUED)

Tentative Identification	Tentative Structure	Temperature of Maximum Formation (C) In N_2	 In Air
Hexachlorobenzene		725	ND
Octachlorostyrene		725	ND
Hexachlorodihydronaphthalene		725	ND
Octachloronaphthalene		725	ND

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[a] Identifications are based on mass spectra alone and are strictly tentative. Standards were not analyzed to confirm these identifications, and in some cases, library spectra were not available for comparison.

[b] ND = not detected on TDAS, with a detection limit of about 2% conversion of parent.

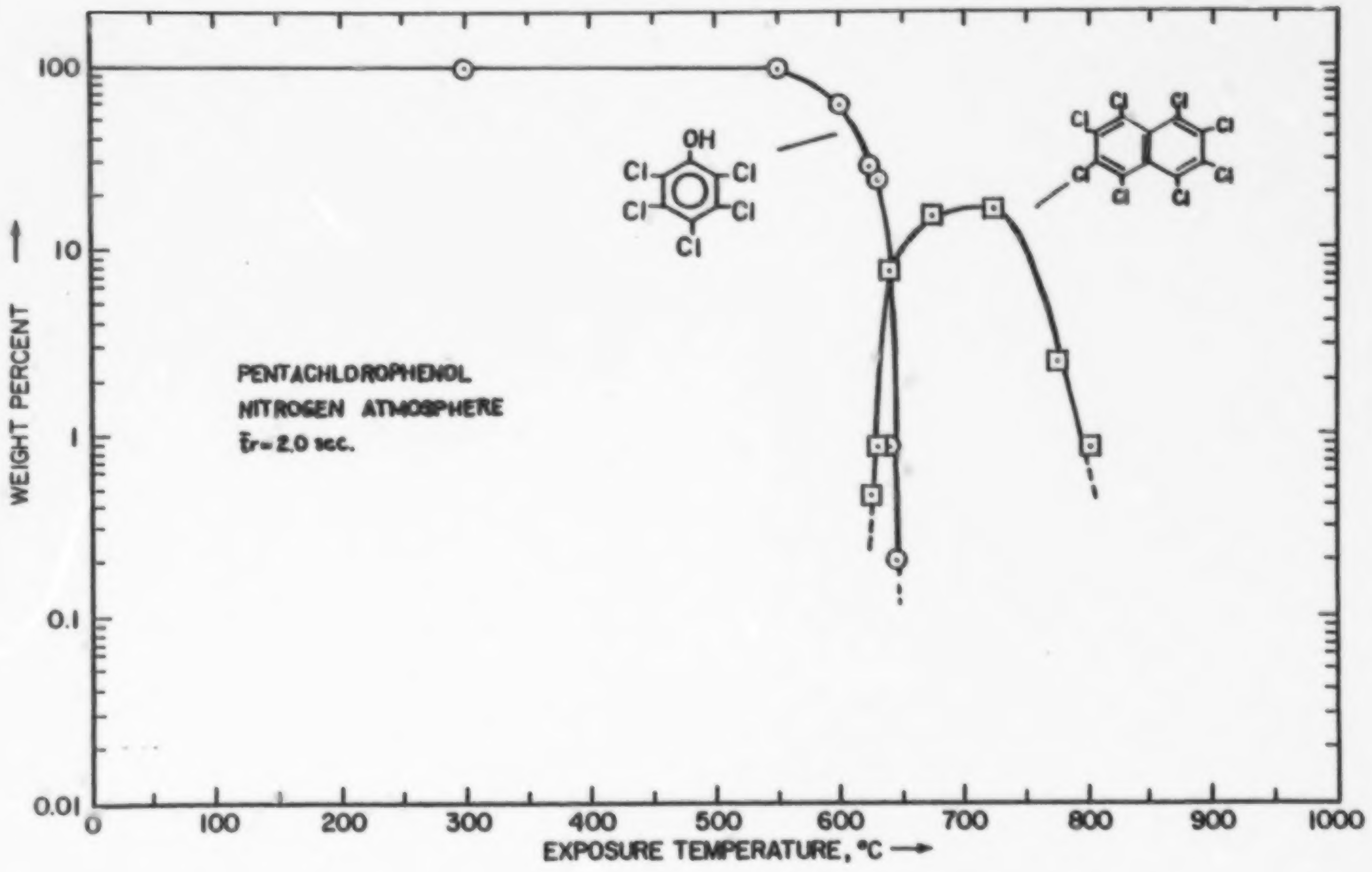


Figure 30. Octachloronaphthalene was the major organic product when PCP was decomposed in a nitrogen atmosphere.

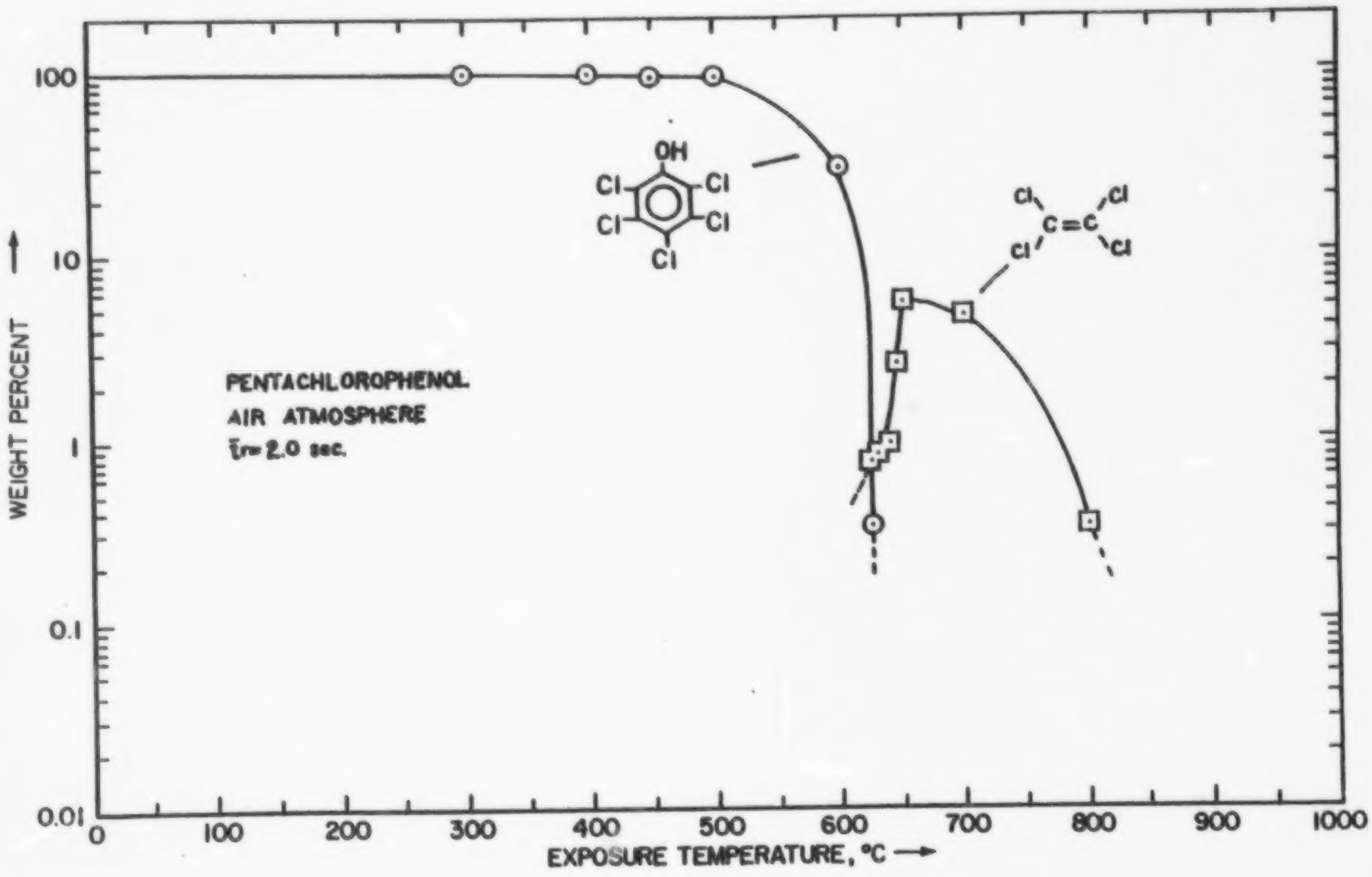


Figure 31. Tetrachloroethylene was the major organic product when PCP was decomposed in an air atmosphere.

species originates in the phenolic OH or in OH radicals which attack the parent material or a decomposition product.

Table 9 includes only the major PICs observed at selected reactor temperatures on the TDAS. It should be noted that the production of octachlorodibenzo-p-dioxin (OCDD) was tentatively identified by retention time on the TDU-GC, and that this identification was confirmed by examining low-level peaks on the TDAS. The maximum yield in air (~1%) was observed at 500°C, while the maximum yield in nitrogen (~1.5%) was seen at 550°C.

It is interesting to compare the thermal decomposition profiles for the three phenolic compounds studied under this program. Pentachlorophenol and nonylphenol were studied as part of the spiked sludge experiments, while phenol was run to fill out the data base and because it was a high-yield PIC from the decomposition of nonylphenol. Thermal decomposition profiles for phenol are shown in Figure 32, while those for nonylphenol and pentachlorophenol were given in Figures 13 and 29, respectively. Temperatures for 99.9% decomposition for these compounds are summarized in Table 10.

Nonylphenol was the most fragile of the three compounds studied, which is significant since it is the phenolic contaminant found in highest concentrations in municipal sludge. However, phenol, which was one of the higher yield PICs from nonylphenol, was the most stable phenolic material tested. This illustrates the importance of establishing incineration conditions which will destroy PICs as well as POHCs.

TABLE 10. SUMMARY OF DECOMPOSITION DATA FOR PHENOLIC COMPOUNDS

	Temperature for 99.9% Decomposition	
Pure Compound[a]	Nitrogen	Air
Nonylphenol	640	510
Pentachlorophenol	640	630
Phenol	760	730

---

[a] Nonylphenol was actually a mixture of isomers; other compounds were pure.

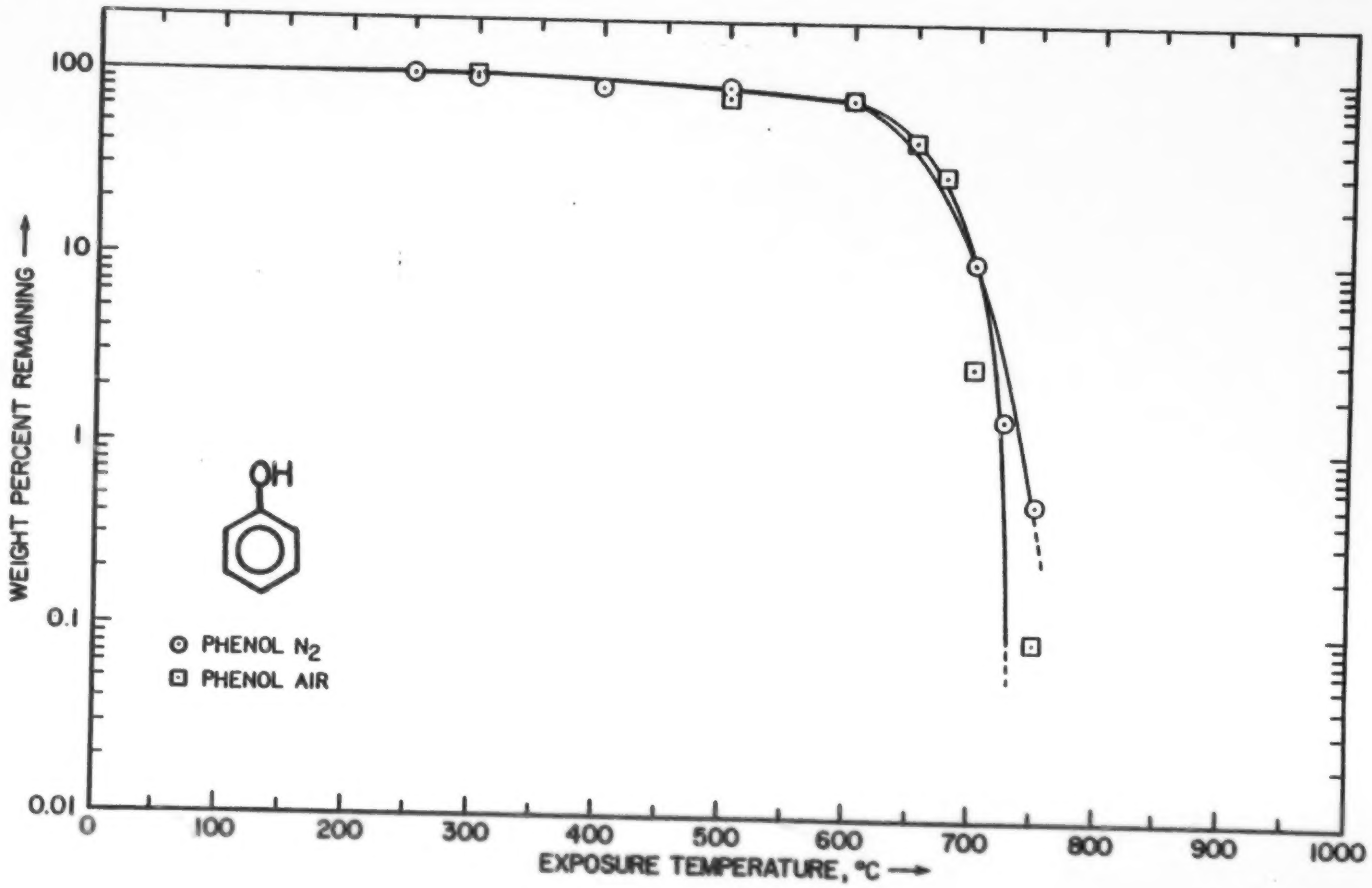


Figure 32. Thermal decomposition profiles for phenol.

SECTION 7

TOXIC EMISSIONS CONTROL IMPLICATIONS

The results of this study indicate that thermal reaction products from partial degradation of the sewage matrix (as opposed to toxic contaminants) may be the source of the largest emission of toxic organics. This suggests that regulations should be based on mass emissions of toxic materials as opposed to a destruction and removal efficiency regulation similar to that promulgated for hazardous waste incinerators [37].

The difficulty with the mass emissions approach lies in deciding which compounds should be controlled. Since the number of Appendix VIII toxic organics is now over 200, the question arises as to which compounds should be regulated and monitored. Stack testing and analysis are very expensive for even limited testing of major inorganic and particulate emissions; if full testing for organics is now required, the cost could be prohibitive. Our data suggest a simplified approach.

Although preliminary, our experimental results suggest that the major emissions from a sewage sludge are likely to be very similar for most sites, i.e., sewage sludge partial decomposition products. This suggests that a limited "hit list" of compounds can be constructed that would be expected to include the highest concentration emissions from any facility. If stack testing is confined to the list and each compound meets the emissions limit set for that compound, then one can feel secure in asserting that other compounds are not being emitted in a quantity that represents a greater threat to the environment. Each compound on the list would have a mass emission limit based on its individual health effects test data. Dispersion modeling could be used to set an emissions limit for a given facility.

Clearly, for such a list to be successful, one would like to be certain that at least one compound on the list has a greater mass emission rate than any compound not on the list. This undoubtedly requires a solid data base on a variety of sludges from different facilities. Also, one must be certain that a trace emission of a highly toxic compound (e.g., TCDD) is not emitted at a level representing a greater environmental threat than a compound on the list. Thus consideration must be given to determining the mass emissions ratio of the "hit list" compounds to toxic trace emissions. In this manner, the hit list compounds would truly be acting as both an "incinerability" and "toxicity" surrogates for all potential emissions.

Still there may be instances where a permit writer would want an additional margin of safety for a suspected highly contaminated, or "problem" sludge. One could then have the option of requiring laboratory thermal decomposition testing of the sludge itself to directly identify the major emissions before conducting full scale compliance testing.

Finally, it would be desirable to have a method for continuous compliance monitoring. We feel that such a monitor could be designed to identify the level of emission of a specific compound or compounds on the hit list (e.g., benzene). The major emission would be verified in the trial burn and then monitored continuously for compliance at a level specified in the operating permit.

It should be pointed out that of currently available continuous monitors, a total hydrocarbon (THC) monitor appears to be the most suitable. Although the response is closely related to the total number of carbon-hydrogen bonds in all of the emitted material and not to a specific toxic emission, it should provide some correlation to toxic emissions. Since the background matrix of the sludge feed is rich in carbon-hydrogen bonds, and this feature of the matrix is very constant, the response of the monitor should be proportional to the destruction efficiency of the sludge.

SECTION 8

REFERENCES

1. Report to Congress on the Discharge of Hazardous Wastes to Public Owned Treatment Works. U.S. EPA Office of Water Regulations and Standards, Washington, D.C., 1986.

2. Second Review of Standards of Performance for Sewage Sludge Incinerators. EPA-450/3-84-010, US-EPA Office of Air Quality Planning and Standards, Research Triangle Park, NC, 1984.

3. W. R. Niessen. Combustion and Incineration Processes: Applications in Environmental Engineering. Marcel Dekker, Inc., New York and Basel, 1978.

4. B. V. Salotto, E. Grossman III, and J. B. Farrell. Elemental Analysis of Wastewater Sludges from 33 Wastewater Treatment Plants in the United States. Presented at Research Symposium on Pretreatment and Ultimate Disposal of Wastewater Solids, New Brunswick, NJ, 1974.

5. A. K. Furr, A. W. Lawrence, S. S. C. Tong, M. C. Grandolfo, R. A. Hofstader, C. A. Bache, W. H. Gutenmann and D. J. Lisk. Multielement and Chlorinated Hydrocarbon Analysis of Municipal Sewage Sludges of American Cities. Environ. Sci & Tech., 10(7):683-687, 1976.

6. R. O. Mumma, D. C. Raupach, J. P. Waldman, S. S. C. Tong, M. L. Jacobs, J. G. Babish, J. H. Hotchkiss, P. C. Wszolek, W. H. Gutenmann, C. A. Bache, and D. J. Lisk. National Survey of Elements and Other Constituents in Municipal Sewage Sludges. Archives of Environmental Contamination and Toxicology, 13(1):75-83, 1984.

7. R. L. Bennett and K. T. Knapp. Characterization of Particulate Emissions from Municipal Wastewater Sludge Incinerators. Environ. Sci. & Tech., 16(12):831-836, 1982.

8. Fate of Priority Pollutants in Publicly Owned Treatment Works. EPA-440/1-82/303, 1982.

9. A Comparison of Studies of Toxic Substances in POTW Sludges. Final report prepared by Camp, Dresser, and McKee for EPA Contract No. 68-02-6403, 1984.

10. A. C. Petrasek, I. J. Kugelman, B. M. Austern, T. A. Pressley, L. A. Winslow, and R. H. Wise. Fate of Toxic Organic Compounds in Wastewater Treatment Plants. Journal WPCF, 55(10):1286-1296.

11. L. M. Naylor and R. C. Loehr. Priority Pollutants in Municipal Sewage Sludge. BioCycle, 23(4):18-22, 1982.

12. Role of Municipal Wastewater Treatment in Control of Toxics. EPA-600/D-82-360, Municipal Environmental Research Laboratory, Cincinnati, 1982.

13. C. Schaffner, P. H. Brunner, and W. Giger. 4-Nonylphenol, a Highly Concentrated Degradation Product of Nonionic Surfactants in Sewage Sludge. Process. Use Sewage Sludge, pp. 168-171, 1984.

14. L. Kravetz, K. F. Guin, W. T. Shebs, and L. S. Smith. Ultimate Biodegradation of an Alcohol Ethoxylate and a Nonylphenol Ethoxylate Under Realistic Conditions. Soap/Cosmetics/Chemical Specialties, 58(4):34-38,40-42,102B, 1982.

15. W. Giger, P. H. Brunner, and C. Schaffner. 4-Nonylphenol in Sewage Sludge: Accumulation of Toxic Metabolites from Nonionic Surfactants. Science, 225(4462):623-625, 1984.

16. P. L. Layman. Commercial Detergent Makers Rely on Technical Service. Chemical and Engineering News, January 1986, pp. 21-42.

17. T. R. Bridle, M. J. Bumbaco, and P. J. Crescuolo. Fate of Polynuclear Aromatic Compounds During Sewage Sludge Incineration. Presented at the 75th Annual WPCF Conference, New Orleans, 1984.

18. Draft Final Test Report - Site 01, Sewage Sludge Incinerator SSI-A, National Dioxin Study, Tier 4: Combustion Sources. Prepared by Radian Corp. for EPA Contract No. 68-03-3148, 1986.

19. Final Draft Test Report - Site 03, Sewage Sludge Incinerator SSI-B, National Dioxin Study, Tier 4:

Combustion Sources. Prepared by Radian Corp. For EPA Contract No. 68-03-3148, 1986.

20. Draft Test Report - Site 12, Sewage Sludge Incinerator SSI-C, National Dioxin Study, Tier 4: Combustion Sources. Prepared by Radian Corp for EPA Contract No. 68-03-3148, 1986.

21. D. S. Duvall and W. A. Rubey. Laboratory Evaluation of the High-Temperature Destruction of Kepone and Related Pesticides. EPA-600/2-76-299, 1976.

22. D. S. Duvall, W. A. Rubey, and J. A. Mescher, Applications of the Thermal Decomposition Analytical System. Presented at the 73rd Annual Meeting of the Air Pollution Control Association, Montreal, Quebec, 1980.

23. B. Dellinger, D. L. Hall, W. A. Rubey, J. L. Torres, and R. A. Carnes. Factors Affecting the Gas-Phase Thermal Decomposition of Chlorinated Aromatic Hydrocarbons. Presented at the Ninth Annual SHWRD Research Symposium, Cincinnati, 1983.

24. B. Dellinger, J. L. Torres, W. A. Rubey, D. L. Hall, and J. L. Graham. Determination of the Thermal Decomposition Properties of 20 Selected Hazardous Organic Compounds. EPA-600/S2-84-138, 1984.

25. W. A. Rubey, B. Dellinger, D. L. Hall, and S. L. Mazer. High-Temperature Gas-Phase Formation and Destruction of Polychlorinated Dibenzofurans. Chemosphere, 14(10):1483-1494, 1985.

26. J. L. Graham, D. L. Hall, and B. Dellinger. Laboratory Investigation of Thermal Degradation of a Mixture of Hazardous Organic Compounds - 1. Environ. Sci. & Tech.,20(7), 1986.

27. F. P. Tully. Laser Photolysis/Laser-Induced Fluorescence Study of the Reaction of Hydroxyl Radical with Ethylene. Chem. Phys. Lett., 96, p. 148, 1983.

28. F. P. Tully and J. E. M. Goldsmith. Kinetic Study of the Hydroxyl Radical-Propene Reaction. Chem. Phys. Lett., 116, p. 345, 1985.

29. J. J. Reuther and W. E. Kaskan. Limiting Equivalence Ratio, Dissociation and Self-Inhibition in Premixed, Quenched, Fuel-Rich Hydrocarbon/Air Flames. 16th Symp.

(Int.) on Combustion, p. 1083, The Combustion Institute, 1977.

30. Y. Beers. Introduction to the Theory of Error. Addison-Wesley Publishing Co. Inc., pp. 26-35, 1957.

31. P. H. Taylor, et al. Thermal Degradation Characteristics of Chlorinated Methane Mixtures. Presented at the 12th Annual Hazardous Waste Research Symposium, Cincinnati, April 21-23, 1986.

32. F. P. Tully, et al. Kinetics of the Reactions of Hydroxyl with Benzene and Toluene. J. Phys. Chem., 85, p. 2262, 1981.

33. J. M. Nicovich et al. Kinetics of the Reactions of the Hydroxyl Radical with the Xylenes. J. Phys. Chem., 85, p. 2913, 19891.

34. R. Atkinson et al. Kinetics of the Reactions of Naphthalene and Biphenyl with OH Radicals and O3 at 294±1 K. Environ. Sci. & Tech., 19, p. 244, 1985.

35. H. W. Biermann et al. Kinetics of the Gas-Phase Reactions of the Hydroxyl Radical with Naphthalene, Phenanthrene, and Anthracene. Environ. Sci. & Tech., 19, p. 244, 1985.

36. A. C. M. Wilson. Insulating Liquids: Their Uses, Manufacture, and Properties. Peter Peregrinus Ltd. (on behalf of the Institution of Electrical Engineers), 144-145, 1980.

37. J. G. Calvert and J. N. Pitts, Jr. Photochemistry. John Wiley and Sons, p. 212, 1966.

38. M. Venugopalan and R. A. Jones. Chemistry of Dissociated Water Vapor. Interscience Publishers, p. 200, 1968.

39. G. A. Castelleon and W. A Noyes. Photochemical Studies. LII. The Nitrous Oxide - Ethane System. J. Am. Chem. Soc., 79, p. 290, 1957.

40. K. Schofield. Critically Evaluated Rate Constants for Gaseous Reactions of Several Electronically Excited Species. J. Phys. Chem. Ref. Data, 8, p. 723, 1979.

41. J. W. Daily. Saturation Effects in Laser-Induced Fluorescence Spectroscopy. Appl. Optics, 16, p. 568, 1977.

42. G. H. Dieke and H. M. Crosswhite. The Ultraviolet Bands of OH. J. Quant. Spectrosc. Radiat. Transfer, 2, p. 97, 1963.

43. A. C. Eckbreth et al. Combustion Diagnostics by Laser Raman and Fluorescence Techniques. Prog. Energy Combust. Sci., 5, p. 291, 1979.

APPENDIX A

THEORY AND INSTRUMENTATION FOR OH REACTIVITY STUDIES

An experimental system has been designed and constructed to reliably measure the high temperature reaction rates of free radicals with hazardous organic compounds. Since equilibrium and kinetic models as well as our flow reactor data indicate that OH may be the dominant reactive species present under most incineration conditions, our initial research has concentrated on the reaction rate determination of OH radicals.

Our overall goal in this research is to clarify results and reaction mechanisms implicated by the global reaction kinetic studies conducted on the flow reactor systems. Once a reliable elementary reaction kinetic data base has been established it may be used along with calculation of the concentrations of radicals, such as OH, in incinerators to make accurate estimates of gas phase destruction efficiencies of POHCs in these full-scale systems. This type of kinetic data may be incorporated into more refined incineration models to improve their accuracy and reliability.

The OH radical was produced by a two-step reaction process. The first step is the photodissociation of nitrous oxide, N_2O, into N_2 and excited oxygen atoms, $O(^1D)$. The second step is the reaction of $O(^1D)$ atoms with water vapor to produce two OH radicals. The photodissociation is caused by irradiance of the gas mixture by a 193 nm wavelength pulse from an Argon Fluoride (ArF) excimer laser.

The expressions for the OH production are:

$$N_2O + h\ (193\ nm) \longrightarrow N_2 + O(^1D)$$

$$H_2O + O(^1D) \longrightarrow 2OH.$$

N_2O is a linear asymmetric molecule with a maximum electronic absorption in the vacuum ultraviolet at 182 nm [37]. The 193 nm wavelength was chosen for photolysis because the absorption band for water vapor is essentially continuous between 143 nm and 186 nm [38], peaking at 165.5 nm. The absorption spectrum for water vapor decreases rapidly above 186 nm [38], thus, 193 nm radiation will photolyze only N_2O.

AT 180 nm, the quantum yield for photodissociation of N_2O is nearly unity [39]. Tully [27] found that for his experimental conditions (5 to 10 mJ/cm^2 of 193 nm radiation), OH conversion was 95% complete in 20 microseconds and more than 95% of the $O(^1D)$ found in the primary photodissociation process was converted to OH.

The experiment is run with excess water vapor (20:1) to provide adequate reaction sites for the $O(^1D)$ atoms, to provide a clean source of OH and to reduce the probability of $O(^1D)$ reactions with N_2O. This also allows the OH concentration to be controlled by the concentration of N_2O.

The OH radical is monitored by laser-induced fluorescence. A simple representation of the excitation and decay process is illustrated in Figure A.1. An atom or molecule is excited from one energy level, typically the ground state, to a higher excited energy level. The excited species then loses energy as it decays to a lower energy level. The method used in this work excites the OH radical at 282.2 nm and monitors the fluorescence (radiative energy loss) at the red-shifted line of 309.0 nm.

Quenching processes compete with fluorescence and provide alternative methods of energy loss. Quenching processes include dissociation, inter- and intramolecular energy transfer and chemical reactions. Quenching rates for excited OH by N_2, H_2O, and He are given in Table A.1 [40].

The energy levels in Figure A.1 can be modeled to predict the concentration of the excited molecule. With thermal equilibration, the total OH concentration can then be attained. A model applicable to this fluorescence detection method has been developed following a similar model presented by Daily [41].

The hydroxyl radical is a prime candidate for application of laser-induced fluorescence as indicated by the following requisites:

1. The OH radical has a well characterized absorption and emission spectrum [42].

TABLE A.1. SUMMARY OF RECOMMENDED RATE CONSTANT VALUES FOR $OH(A^2\Sigma)$, 300 K, (cm^3/molec-s)

M	$k_{electronic}$	$k_{vibrational}(N'=0,1)$[a]	$k_{rotational}$[b]
H_2O	$5.0(+2.0,-2.0)x10^{-10}$	FAST	$2x10^{-10}$
N_2	$2.2(+1.8,-1.2)x10^{-11}$	$1.7x10^{-10}$	$4x10^{-10}$
He	$1.0x10^{-14}$	$1.0x10^{-12}$	$1x10^{-11}$

[a] A function of N'

[b] N_o pronounced N' dependence

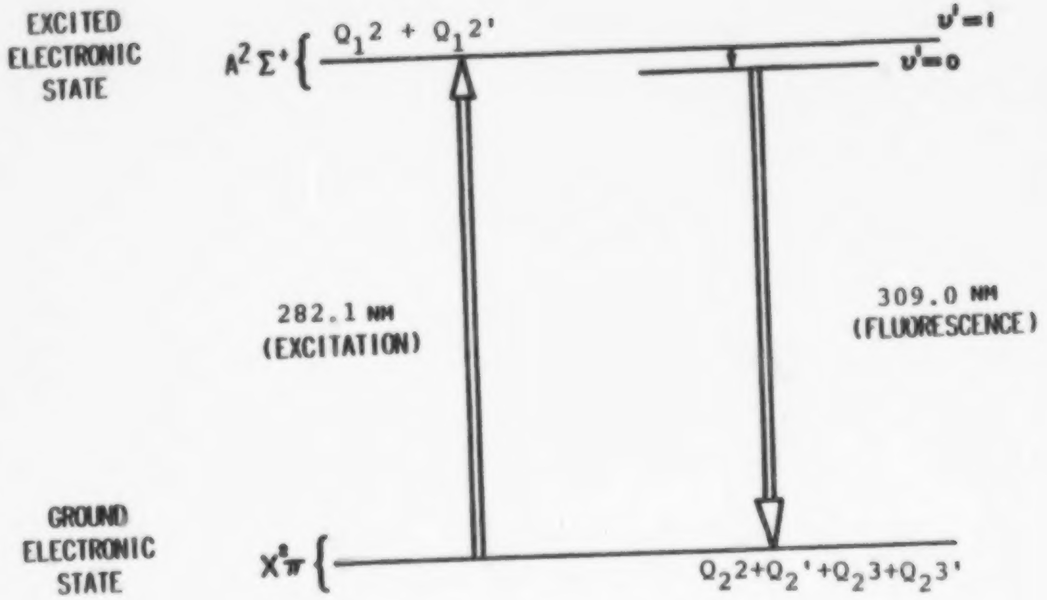

EXCITED ELECTRONIC STATE
$A^2\Sigma^+$
$Q_1 2 + Q_1 2'$
$v'=1$
$v'=0$
282.1 NM (EXCITATION)
309.0 NM (FLUORESCENCE)
GROUND ELECTRONIC STATE
$X^2\pi$
$Q_2 2 + Q_2 2' + Q_2 3 + Q_2 3'$

Figure A.1. Energy levels of the OH radical pertaining to the laser-induced fluorescense experiment.

2. OH can be optically excited without causing photodissociation of the O-H bond.

3. The absorption and emission spectra are within the ranges of available laser and detection systems.

4. The rates of radiative decay of the excited states of OH are known (A_{21} of $A^2\Sigma^+$: 1.32×10^6 s^{-1} [40]).

5. The difficulties associated with quenching can be circumvented, thus allowing detection of the radiative decay.

Daily (41) has presented two methods of measuring the concentration of species by laser-induced fluorescence. The first method involves observing the temporal behavior of the fluorescence while the second involves time-averaged measurements of the fluorescence power. The second method was chosen because it is more suited to the electronics presently accessible.

For the time averaged measurement, Daily's expression for the fluorescence power is given [41] by:

$$S_F = h(\frac{c}{\lambda}) (\frac{A_{21}}{4\pi}) \varepsilon\Omega V_C(N_2/N_0)I_{L_\nu} N_1$$

where:

A_{21} = radiative lifetime of OH(s^{-1})
ε = light collection efficiency
V_C = collection volume (cm^3)
Ω = solid collection angle (steradians)
N_2/N_0 = fraction of molecules fluorescing
I_{L_ν} = probe laser power density per unit bandwidth
N_1 = concentration of absorbing OH radicals (cm^{-3}).

The critical parameter in the expression is the fraction of molecules fluorescing. This parameter accounts for reduction in the attainable OH fluorescence due to quenching (see Figure A.1). N_2/N_0 has been estimated with the development of a three level model similar in nature to that of Pipmeier [43]. Application of this model allows accurate determination of the OH concentration for a given fluorescence current. This is of critical importance in that chlorocarbon-hydroxyl concentration ratios can then be established to allow pseudo-first order kinetics to prevail during data collection.

The experimental test system consists of five interdependent components: (1) a test cell and temperature control system, (2) the sample delivery system, (3) the pump laser system, (4) the probe laser system, and (5) the detection/measurement system.

The test cell is a specially designed quartz cell which allows gas reactants to be heated, irradiated with laser beams, and observed. Figure A.2 is a schematic of the cell. The reaction cell is a cylindrical quartz tube fitted with four arms (terminated with suprasil windows) to accommodate laser beam entrance and exit. One end of the cell was designed to feed a laminar uniform flow of gas through the cell volume. The other end has a side port gas exit and terminates with a quartz lens.

The cell flow characteristics enable the gas entering the cell to be heated in a square-wave temperature profile. This is accomplished with minimum residence time and essentially isothermal conditions through a volume which envelopes the reaction zone. The gas flow is at the test temperature from the time it enters the cell until after it passes beyond the reaction volume. The time at temperature up to the center of the reaction zone based on the volumetric flow rate is 0.875 seconds. The materials chosen must not undergo major decomposition for this amount of time. The chlorocarbon samples chosen for this work have known thermal decomposition temperatures [31].

The cell gas flow velocity of 4 cm/sec was chosen to ensure that each excimer/probe pulse pair sees a fresh gas sample. This "slow flow" condition is necessary to avoid buildup of reaction products and complication of data analysis due to secondary reactions.

For this experiment the temperature of the interior of the cell is adjusted by resistive heaters. The cell is insulated and enclosed in an aluminum box. In order to maintain a moderate cell outer skin temperature beneath the photomultiplier tube, PMT, a water cooling coil was installed between the cell's insulation and the inner surface of the box.

The gas delivery system is composed of a pyrex mixing bulb preceded by a manifold with controlled gas inlets for nitrous oxide, water vapor, helium carrier gas, and organic samples. The purpose of this configuration is to thoroughly mix the gas constituents before they enter the cell and thus allow selectable and repeatable compositions. The gas mix and delivery system is illustrated in Figure A.3. Three differential flow controllers are used to meter the helium, helium/water vapor and nitrous oxide gas flows. Water vapor is introduced into the system by bubbling controlled flows of helium through a heated water filled bulb. The organic sample is prepared in a 1 liter glass bulb and introduced by injection from a 10 cm^3 gas-tight syringe. The current configuration is

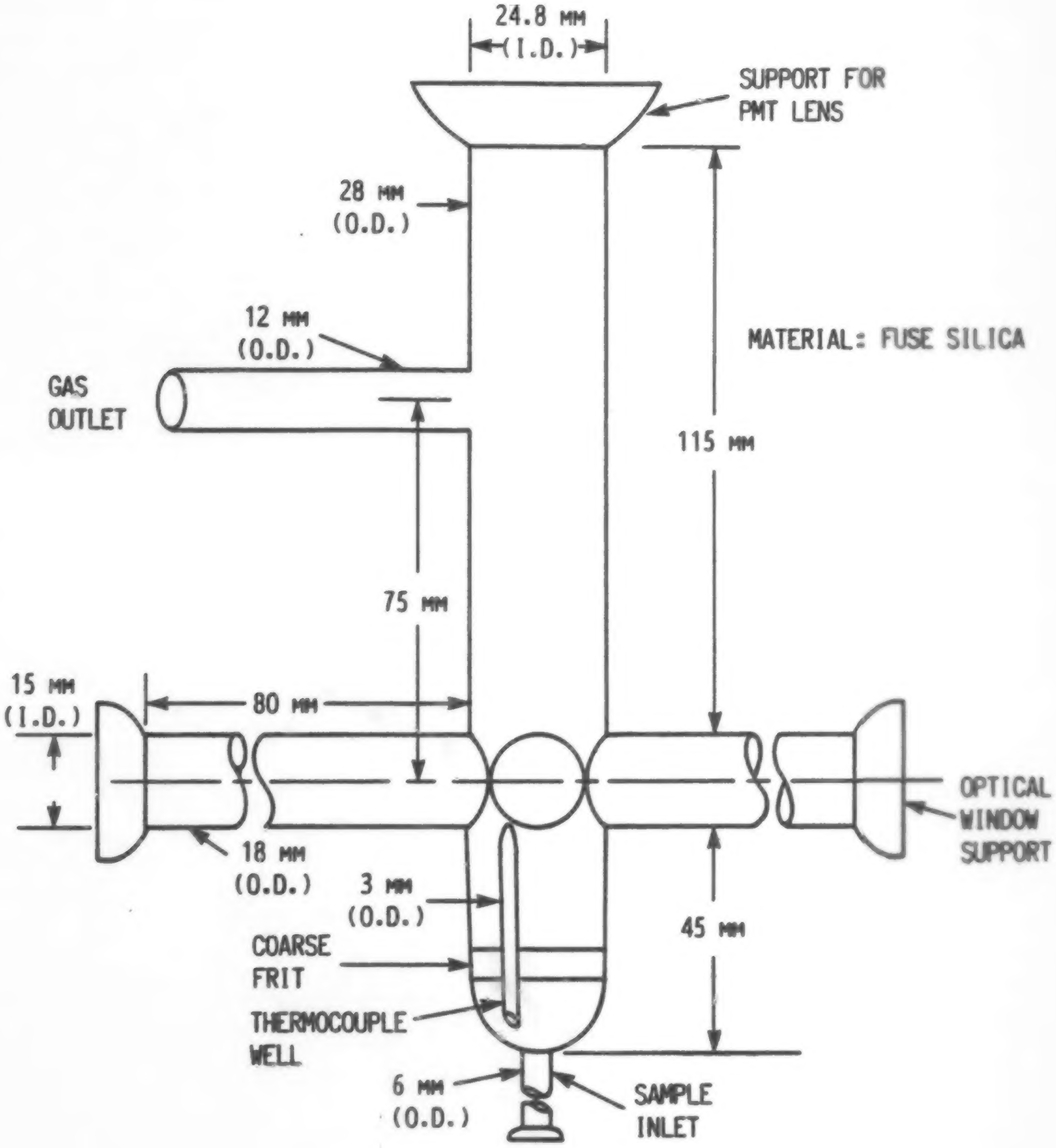

24.8 MM
(I.D.)
SUPPORT FOR
PMT LENS
28 MM
(O.D.)
12 MM
(O.D.)
GAS
OUTLET
MATERIAL: FUSE SILICA
115 MM
75 MM
15 MM
(I.D.)
80 MM
OPTICAL
WINDOW
SUPPORT
18 MM
(O.D.)
3 MM
(O.D.)
45 MM
COARSE
FRIT
THERMOCOUPLE
WELL
6 MM
(O.D.)
SAMPLE
INLET

Figure A.2. Laser test cell design.

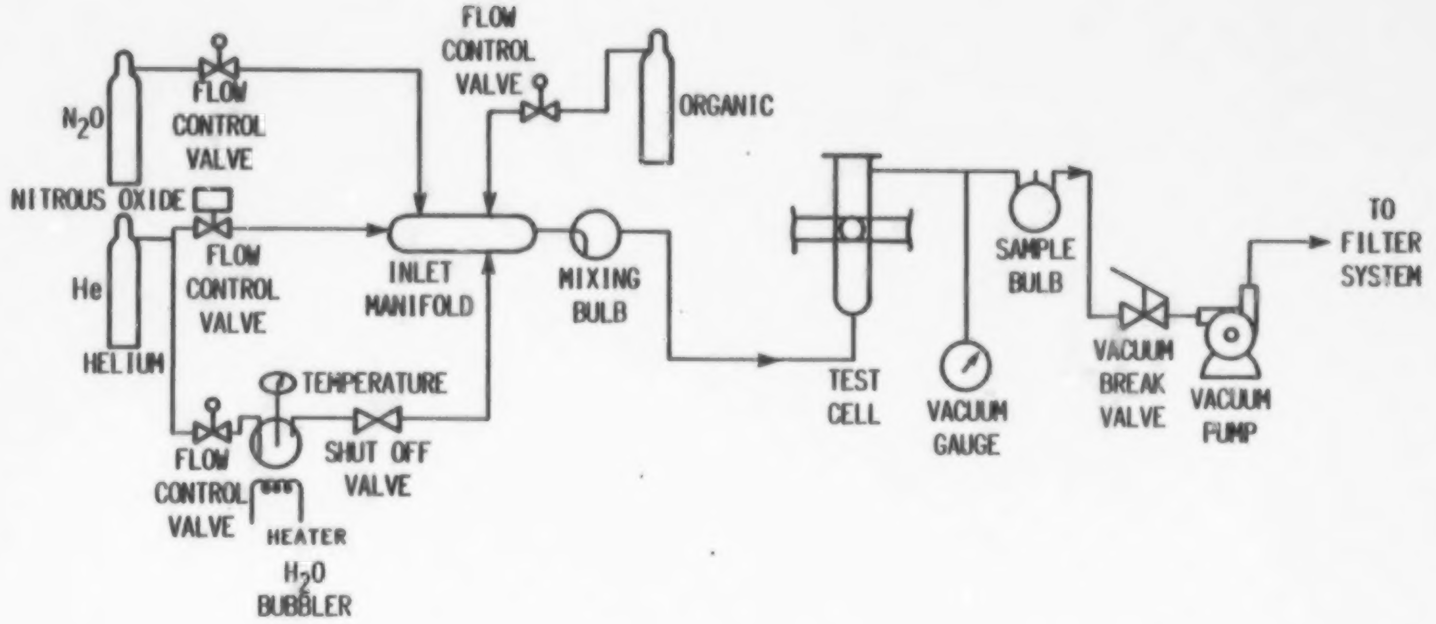

FLOW
CONTROL
VALVE
N_2O
FLOW
CONTROL
VALVE
ORGANIC
NITROUS OXIDE
He
HELIUM
FLOW
CONTROL
VALVE
INLET
MANIFOLD
MIXING
BULB
TEST
CELL
VACUUM
GAUGE
SAMPLE
BULB
VACUUM
BREAK
VALVE
VACUUM
PUMP
TO
FILTER
SYSTEM
TEMPERATURE
FLOW
CONTROL
VALVE
SHUT OFF
VALVE
HEATER
H_2O
BUBBLER

Figure A.3. Sample-gas delivery system.

setup for gas samples and liquids of sufficient volatility which will maintain their integrity without special handling. A sample bulb downstream of the reaction zone allows extraction of organic samples for GC/HFID testing (in the absence of OH) when thermal decomposition and/or laser-induced photolysis is a concern. The cell discharge is connected to a vacuum pump. This system allows the cell to be evacuated (<0.1 torr) before each experimental run and allows control of the cell pressure.

The pump laser used in the experiment was charged with an Argon Fluoride, ArF, mixture. It has the capability to produce a 20 mJ/pulse output at 10 hertz and a 2 watt output at 100 hertz. This ArF laser emits a beam of ultraviolet radiation at 193 nm. The beam is unprocessed from the laser to the cell except for an aperature to skim the extremes of the beam and allow a homogeneous (4 mm x 14 mm) beam with a power density of 5 to 15 mJ/cm^2 to enter the cell. Normal operation is at 10 hertz.

The probe beam system includes all the components necessary to produce and deliver a 282.2 nm beam to the cell's reaction zone. The elements of the system are a niodium-yttrium-aluminum-garnet (Nd:YAG) pulsed laser, an optically pumped dye laser, a second harmonic generator, and a turning prism.

A Nd:YAG, Q-switched, pulsed laser is the first component in the tandem laser system. The output is optimized at 10 hertz and is linearly polarized. The primary beam is an infrared 1.06 m output which is externally frequency doubled to a visible green line, at 532 nm. A temperature controlled crystal is used to generate the 532 nm wavelength. The choice of dye (Rhodamine 590) determines the output wavelength of the dye laser system. The exit beam from the dye laser was at a wavelength of 564.4 nm and was frequency doubled (282.2 nm) by a second harmonic generating crystal for excitation of OH radicals.

The beam emanating from the doubling crystal is a composite of 282.2 nm and 564.4 nm light and is separated by a UG-11 colored glass filter prior to entering the reaction cell. The 282.2 line was chosen based on the calculation of the ground state population in a given rotational level versus temperature. The optical system used is illustrated in Figure A.4.

The control of scattered light was of utmost importance in the fluorescence detection. Thus, beam blocks and light tunnels were installed to contain beam reflections and apertures were installed to control the beam diameter and second reflections. Quartz is a good transmitter of ultraviolet light and any portion of the 282.2 nm light incident on the cell

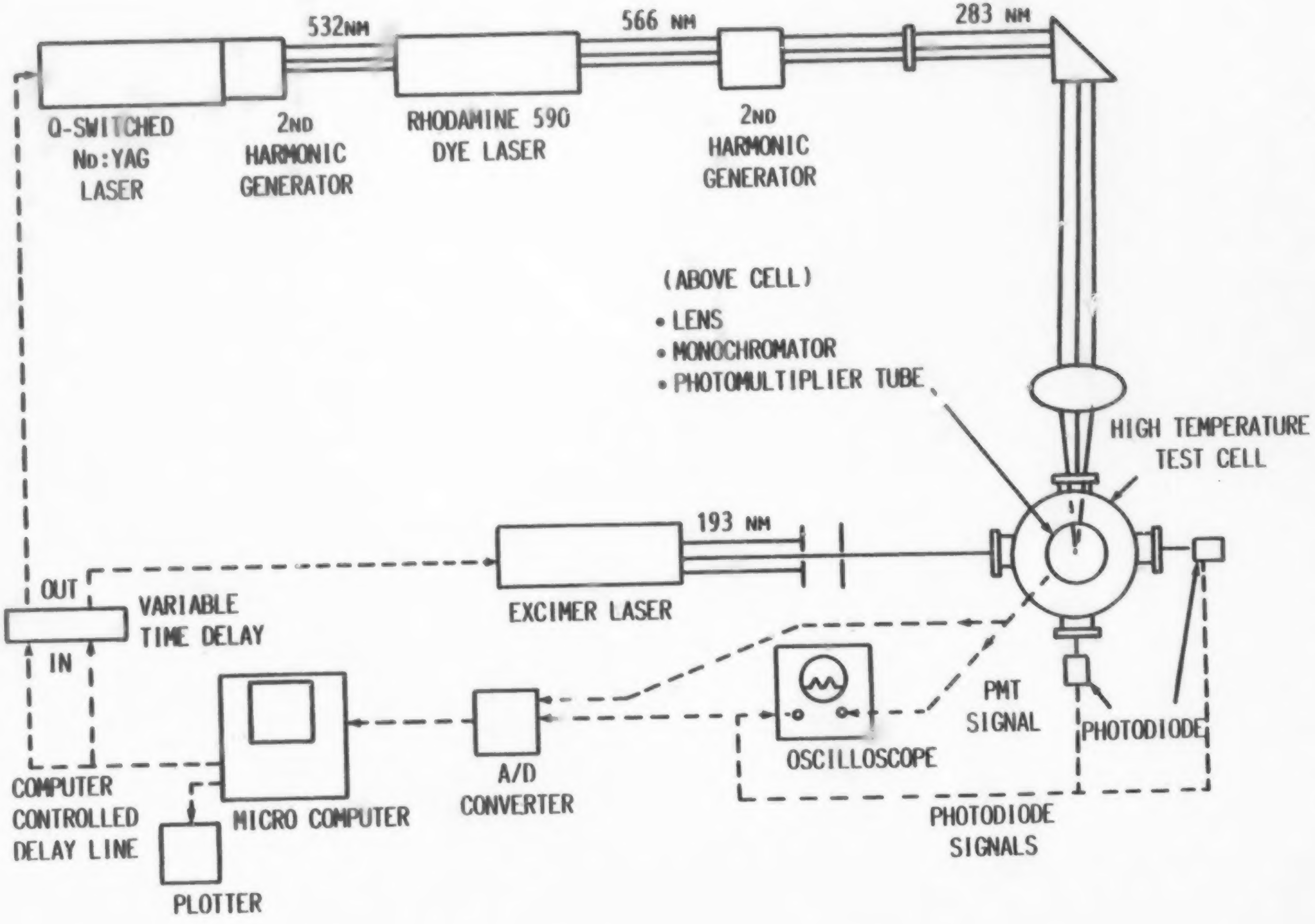

532NM
566 NM
283 NM
Q-SWITCHED
ND:YAG
LASER
2ND
HARMONIC
GENERATOR
RHODAMINE 590
DYE LASER
2ND
HARMONIC
GENERATOR
(ABOVE CELL)
• LENS
• MONOCHROMATOR
• PHOTOMULTIPLIER TUBE
HIGH TEMPERATURE
TEST CELL
193 NM
OUT
IN
VARIABLE
TIME DELAY
EXCIMER LASER
PMT
SIGNAL
PHOTODIODE
OSCILLOSCOPE
PHOTODIODE
SIGNALS
COMPUTER
CONTROLLED
DELAY LINE
MICRO COMPUTER
A/D
CONVERTER
PLOTTER

Figure A.4. Hydroxyl radical generation and detection system.

walls contributed to noise being detected by the photomultiplier tube, PMT.

Although the OH fluorescence is 4 steradians, the collection system only captures a portion of the signal through the top of the cell. The top of the cell has an O-ring bell to which a quartz lens is attached. This lens is used to image the reaction volume on the photocathode window of the photomultiplier tube, PMT. The PMT is equipped with a UG-11 colored glass filter and bandpass filter (308.5 nm, 11 nm fwhm) to isolate the OH fluorescence. The signal conditioning consists of conversion to a voltage source, time-discriminant multichannel amplification, and analog to digital (A/D) conversion before being fed into an Apple IIe microcomputer.

To acquire OH signals as a function of time, a time delay system consisting of a time delay generator and photodetectors for monitoring the firing of the two laser pulses was designed and built. The computer generates an output pulse to a delay generator circuit which interfaces with the trigger inputs for the excimer and Nd:YAG lasers. The delay time between the firing of the excimer and Nd:YAG may be varied from the computer keyboard. A typical OH decay scan begins 1 ms after the excimer pulse and is terminated 40 ms after excimer pulse.

APPENDIX B

INSTRUMENTATION FOR GLOBAL THERMAL DECOMPOSITION STUDIES

The University of Dayton Research Institute has designed and constructed three instrumentation systems that can be used to study the high-temperature thermal decomposition of organic materials under highly controlled conditions. All three systems consist of thermal decomposition units interfaced with an in-line gas chromatograph (GC) or gas chromatograph-mass spectrometer (GC-MS). The thermal units are comprised of a control console, a sample introduction region, a high-temperature reactor, and heated transfer lines. Effluents from the thermal reactor (both remaining starting materials and thermal reaction products) are cryogenically trapped at the head of the in-line gas chromatographs, and then are analyzed by GC-MS (for both qualitative and quantitative analysis) or GC (for quantitative analysis only). Two of these thermal systems were utilized for the sewage sludge program; construction of the third (a more flexible system) was completed as this program was approaching its conclusion, and will not be further discussed here.

The Thermal Decomposition Analytical System (TDAS) consists of a controlled, high-temperature, quartz reactor with a dedicated in-line LKB 2091 GC-MS to determine the thermal stability of organic materials in addition to identification of thermal reaction products. Figure B.1 shows a block diagram of the TDAS, and Figure B.2 is an artist's rendering of this assembled instrumentation system. Basically, the TDAS consists of: (1) a special thermal decomposition unit with its own dedicated instrumentation assembled in a control console, (2) an in-line high-resolution gas chromatograph (HRGC) which is coupled to (3) a mass-spectrometer which in turn is served by (4) a dedicated mini-computer system.

The Thermal Decomposition Unit-Gas Chromatographic (TDU-GC) system uses essentially the same thermal decomposition unit design but incorporates a high-resolution gas chromatograph with flame ionization and other detectors. The TDU-GC has a Varian 4600 GC and a dedicated CDS 401 data terminal. A block diagram of the TDU-GC is given in Figure B.3, while an artist's rendering of the system is provided in Figure B.4.

A key component of both the TDAS and the TDU-GC is the precisely controlled high-temperature reactor. The major

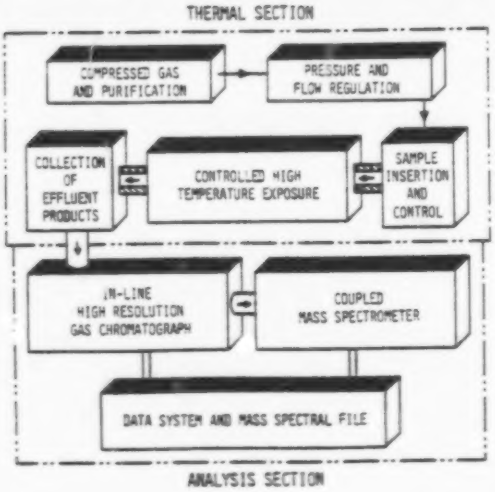

THERMAL SECTION
COMPRESSED GAS AND PURIFICATION
PRESSURE AND FLOW REGULATION
COLLECTION OF EFFLUENT PRODUCTS
CONTROLLED HIGH TEMPERATURE EXPOSURE
SAMPLE INSERTION AND CONTROL
IN-LINE HIGH RESOLUTION GAS CHROMATOGRAPH
COUPLED MASS SPECTROMETER
DATA SYSTEM AND MASS SPECTRAL FILE
ANALYSIS SECTION

Figure B.1. Block diagram of the TDAS.

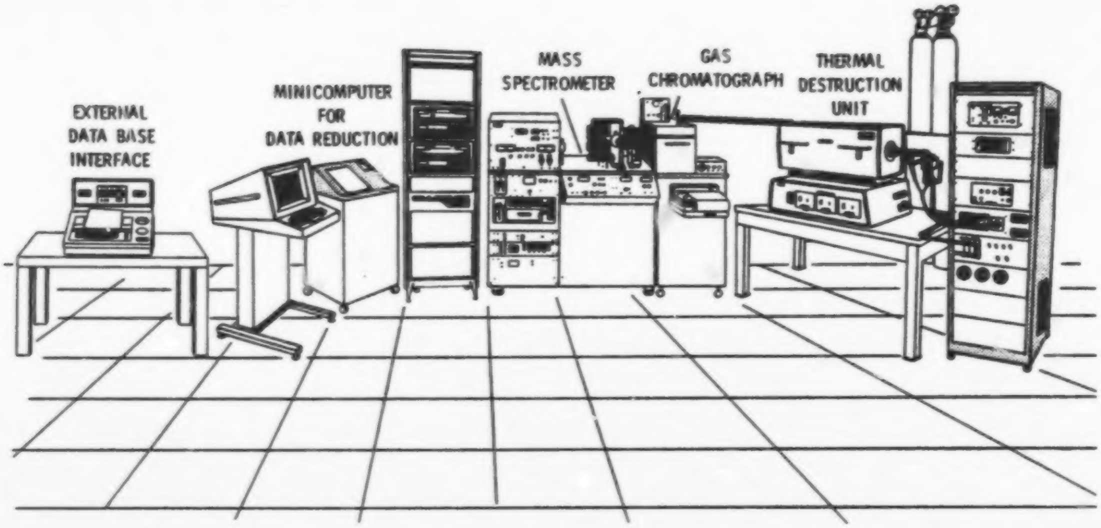

EXTERNAL DATA BASE INTERFACE
MINICOMPUTER FOR DATA REDUCTION
MASS SPECTROMETER
GAS CHROMATOGRAPH
THERMAL DESTRUCTION UNIT

Figure B.2. Artist's Rendering of Assembled TDAS.

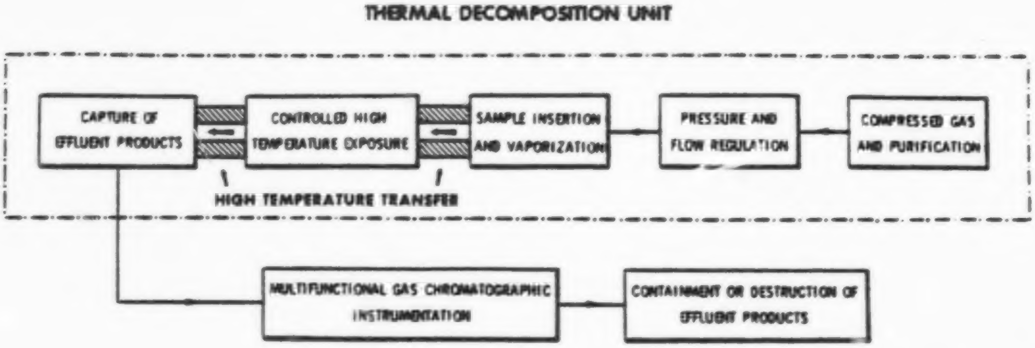

THERMAL DECOMPOSITION UNIT
CAPTURE OF EFFLUENT PRODUCTS
CONTROLLED HIGH TEMPERATURE EXPOSURE
SAMPLE INSERTION AND VAPORIZATION
PRESSURE AND FLOW REGULATION
COMPRESSED GAS AND PURIFICATION
HIGH TEMPERATURE TRANSFER
MULTIFUNCTIONAL GAS CHROMATOGRAPHIC INSTRUMENTATION
CONTAINMENT OR DESTRUCTION OF EFFLUENT PRODUCTS

Figure B.3. Block diagram of TDU-GC.

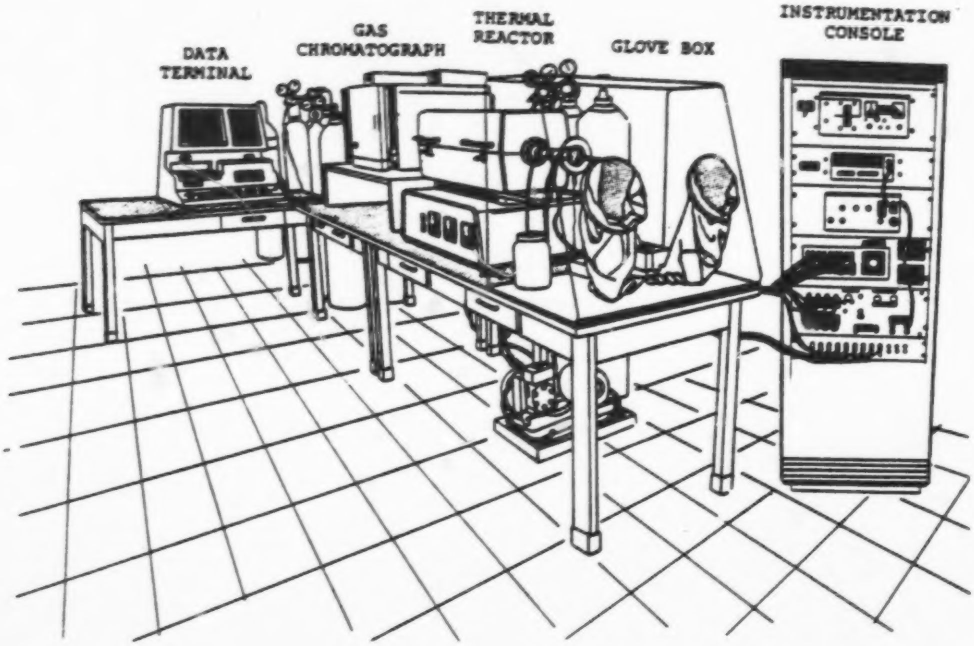

DATA TERMINAL
GAS CHROMATOGRAPH
THERMAL REACTOR
GLOVE BOX
INSTRUMENTATION CONSOLE

Figure B.4. Artist's rendering of assembled TDU-GC.

portion of the reactor consists of a narrow-bore (nominal 1 mm ID) quartz tube flowpath in a race-track configuration (3.5 cycles, 1 meter in length). The quartz tube reactor assembly fits into a high-temperature three zone Lindberg furnace designed for continuous operation at temperatures up to 1200°C with control to ±1°C. Fine bore entrance and exit tubes transport the sample rapidly into and out of the central portion of the reactor. This flow design provides a narrow residence time distribution and square wave exposure temperature profile. The inert surface provided by the all-quartz construction minimizes wall reactions.

Both of these systems can be used for conducting precise laboratory-scale experiments and evaluating the effects of major decomposition variables, such as exposure temperature, residence time, reaction atmosphere, and sludge composition.

Testing using these systems is accomplished through a series of well-controlled and precisely-timed procedures. To initiate a test, samples are introduced using appropriately designed probes, and volatile sample components are gradually vaporized in a flowing gas stream (i.e., nitrogen, air, or nitrogen/oxygen mixtures). The vaporized sample is swept through a controlled, high-temperature tubular reactor where it undergoes thermal decomposition. The thermal decomposition products and the remaining parent compound are then swept into a high-resolution gas chromatograph for analysis. The sample insertion chamber, the reactor, and the entire transport system are fabricated of fused quartz to minimize surface interaction with the samples.

The TDU-GC is typically used to generate the quantitative information on parent decomposition and formation of thermal reaction products. This is accomplished by conducting tests at ten to twelve reactor temperatures between 300°C and 1000°C (atmosphere and residence time being held constant), and then plotting the percent remaining of the parent and/or the product yield as a function of temperature. Figure B.5 depicts typical chromatograms obtained for a spiked sludge at a nondegradative reactor temperature (300°C) versus a highly degradative temperature (1000°C), while Figure B.6 depicts profiles for the decomposition of a parent material and the formation/ destruction of a thermal reaction product.

After the TDU-GC data is complete, the TDAS is typically used for the identification of thermal reaction products at selected reactor temperatures.

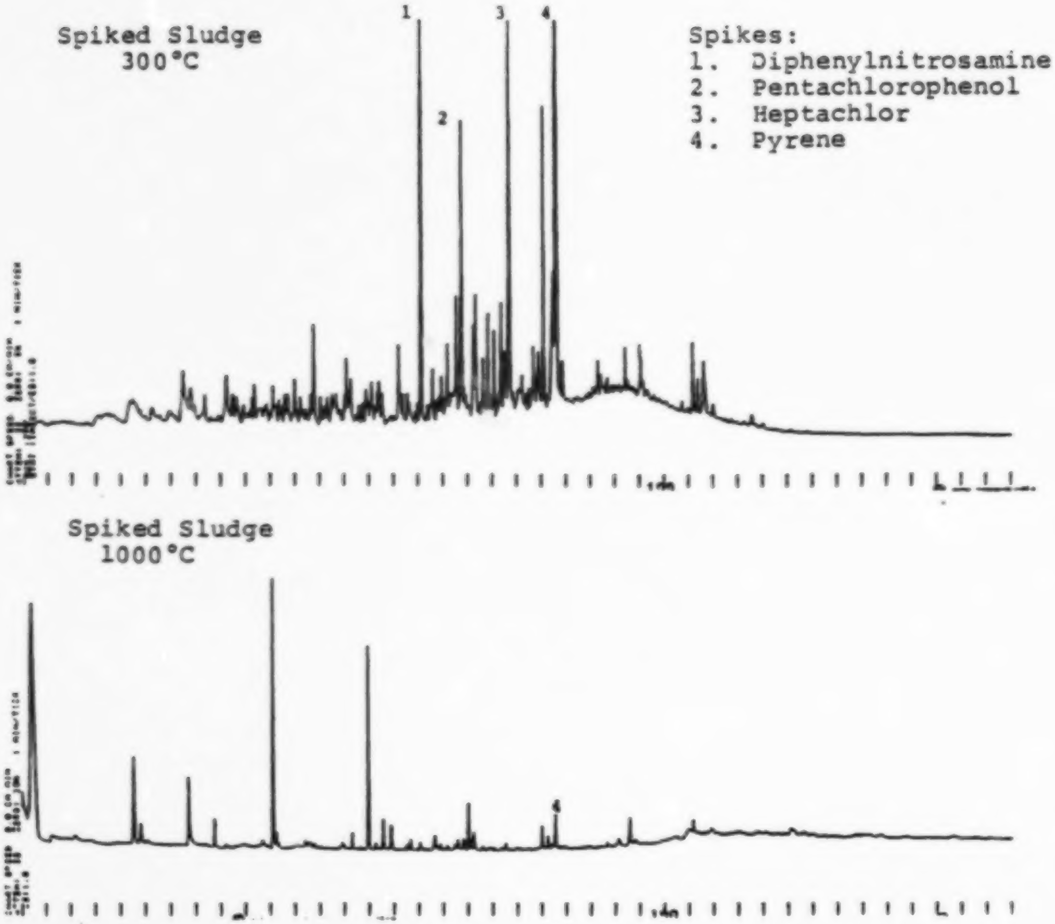


Figure B.5. TDU-GC chromatograms obtained at two reactor temperatures during thermal decomposition testing of spiked sludge. Products at 1000°C were later identified using TDAS.

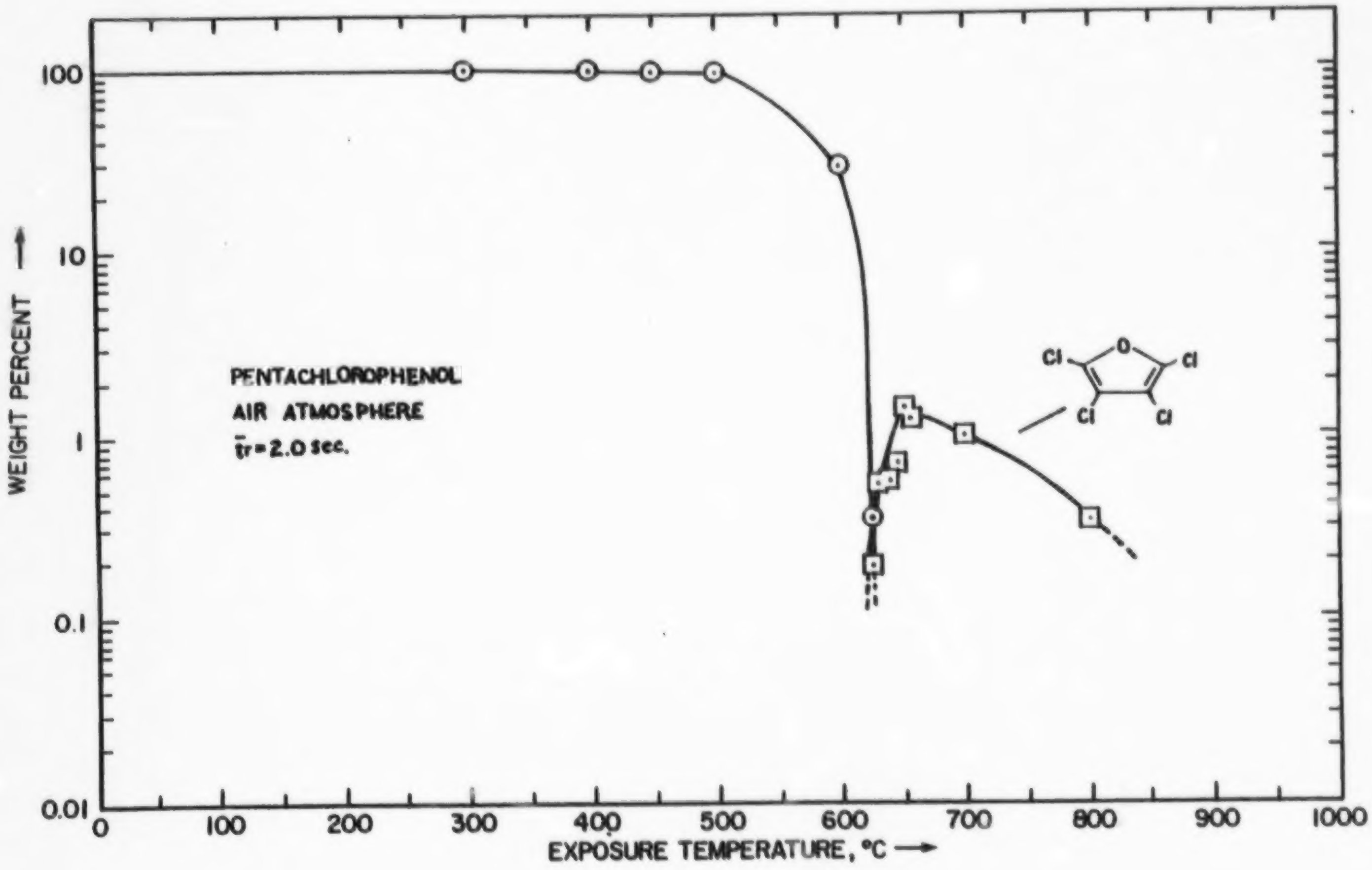


Figure B.6. Thermal decomposition profile for pentachlorophenol and formation/destruction profile for thermal reaction products.

There are several advantages in using these thermal decomposition systems for identifying the most probable emissions from sewage sludge incineration. Specifically:

- These systems have already been constructed, tested, and used successfully;
- The variables affecting thermal decomposition can be well controlled and measured;
- To facilitate valid comparisons, materials can be tested under well-defined reproducible standard conditions;
- Both quantitative and qualitative data can be obtained relatively quickly and easily; and
- The capability of the in-line analytical instrumentation to trap thermal reaction products obviates the need for time-consuming sample extractions and other manipulations.

APPENDIX C

PRODUCTS OF INCOMPLETE COMBUSTION FOR SPIKED SLUDGES AND SPIKING MIXTURES

TABLE C-1. MAJOR THERMAL DECOMPOSITION PRODUCTS FROM COMPOSITE A SPIKED SLUDGE

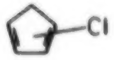
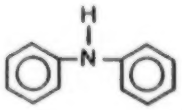
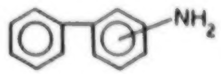
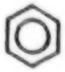
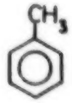
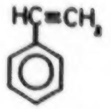
Tentative Identification[a]	Structure[b]	Confidence Factor[c]	500°C		600°C		650°C		800°C	
			N_2	Air	N_2	Air	N_2	Air	N_2	Air
Chlorocyclopentadiene		2	x[d] (2)	--	xx (2)	--	--	--	--	NOT RUN
Diphenylamine or Aminobiphenyl	 or 	1	xx	xx	xx	--	xx	--	--	
Benzene		1	--	--	x	--	x	x	xx	
C_7-Alkene or C_7-Cycloalkane or C_6-Unsaturated ketone	C_7H_{14} or $C_6H_{10}O$	2	--	--	x	--	--	--	--	
Toluene		1	--	--	x	--	x	x	x	
C_8-Alkene or C_8-Cycloalkane or C_7-Unsaturated ketone	C_8H_{16} or $C_7H_{12}O$	2	--	--	x	--	--	--	--	
Styrene		1	--	--	--	--	x	x	x	

TABLE C-1 (CONTINUED)

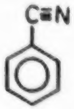
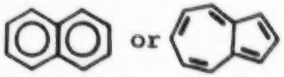
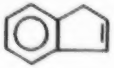
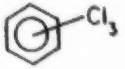
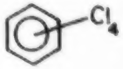
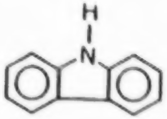
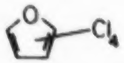
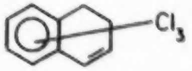
Tentative Identification[a]	Structure[b]	Confidence Factor[c]	500°C N$_2$	500°C Air	600°C N$_2$	600°C Air	650°C N$_2$	650°C Air	800°C N$_2$	800°C Air
Cyclopentadiene or C_5-ene-yne	C_5H_6	1	--	--	--	--	--	--	x	NOT RUN
Benzonitrile		1	--	--	--	--	--	x	x	
Naphthalene or Azulene		1	--	--	--	--	--	--	x	
1H-Indene		1	--	--	--	--	--	--	x	
Trichlorobenzene		1	--	--	--	--	--	--	x	
Tetrachlorobenzene		1	--	--	--	--	--	--	x	
9H-Carbazole		1	--	x	--	x	--	--	x	

TABLE C-1 (CONCLUDED)

Tentative Identification[a]	Structure[b]	Confidence Factor[c]	500°C		600°C		650°C		800°C	
			N_2	Air	N_2	Air	N_2	Air	N_2	Air
Tetrachlorofuran		2	--	x	--	x	--	--	--	NOT RUN
Trichlorodihydronaphthalene		2	--	x	--	--	--	--	--	
Unknown	?	N/A	--	--	x	--	--	--	--	

C-1

FOOTNOTES

[a] Identifications are considered tentative because actual standards were not analyzed to confirm them. Other isomers are possible.

[b] Possible structures are presented. Other isomers are possible in some cases.

[c] Confidence factors:

1 = Spectral match found in EPA-NIH library.
2 = No library match found; manual spectral interpretation was performed with high confidence in results.
3 = No library match found; manual spectral interpretation yielded results which may be subject to error.

N/A = Not applicable.

[d] Results codes:

x = Compound was detected as a major thermal decomposition product.
xx = Compound was one of the largest peaks in the thermal decomposition run.
x (number) = More than one isomer of a given compound was detected. The number of isomers is given in parentheses.
xx (number) = More than one isomer of the given compound was detected and the summed peaks constituted one of the highest yield thermal decomposition products.
-- = Compound was not a major thermal decomposition product.

TABLE C-2. MAJOR THERMAL DECOMPOSITION PRODUCTS FROM COMPOSITE A SPIKE SOLUTION

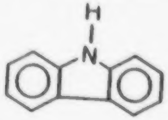
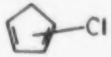
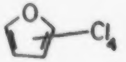
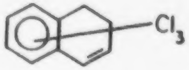
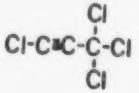
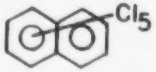
Tentative Identification[a]	Structure[b]	Confidence Factor[c]	400°C		500°C		650°C		800°C		1000°C	
			N_2	Air	N_2	Air	N_2	Air	N_2	Air	N_2	Air
9H-Carbazole		1	NOT RUN	x[d]	x	x	NOT RUN	--	xx	NOT RUN	--	NOT RUN
Chlorocyclopentadiene		2		--	x (2)	xx (2)		--	--		--	
Tetrachlorofuran		2		--	--	x		x	--		--	
Trichlorodihydronaphthalene		2		--	--	x		--	--		--	
Dichloroacetylene	Cl-C≡C-Cl	1		--	--	--		x	--		--	
Tetrachloropropyne	 $Cl\text{-}C\equiv C\text{-}CCl_3$	2		--	--	--		x	--		--	
Pentachloronaphthalene		2		x	x	--		--	x		--	

TABLE C-2 (CONTINUED)

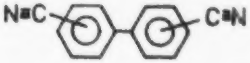
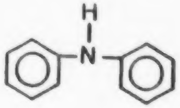
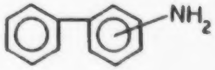
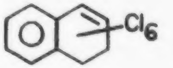
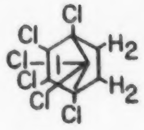
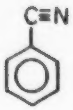
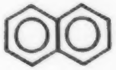
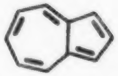
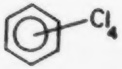
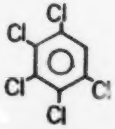
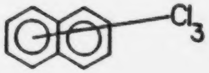
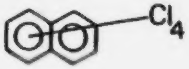
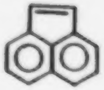
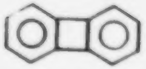
Tentative Identification[a]	Structure[b]	Confidence Factor[c]	400°C		500°C		650°C		800°C		1000°C	
			N_2	Air	N_2	Air	N_2	Air	N_2	Air	N_2	Air
Biphenyldicarbonitrile		1	NOT RUN	--	--	--	NOT RUN	x	--	NOT RUN	--	NOT RUN
Diphenylamine or Aminobiphenyl	 or 	1		xx	xx	--		--	--		--	
Hexachlorodihydro-naphthalene		2		--	x	--		--	--		--	
Hexachloromethano-cyclohexene		3		--	x	--		--	--		--	
Benzonitrile		1		--	--	--		--	x		x	
Naphthalene or Azulene	 or 	1		--	--	--		--	x		--	

TABLE C-2 (CONCLUDED)

Tentative Identification[a]	Structure[b]	Confidence Factor[c]	400°C N_2	400°C Air	500°C N_2	500°C Air	650°C N_2	650°C Air	800°C N_2	800°C Air	1000°C N_2	1000°C Air
Tetrachlorobenzene		1	NOT RUN	--	--	--	NOT RUN	--	x	NOT RUN	--	NOT RUN
Pentachlorobenzene		1	NOT RUN	--	--	--	NOT RUN	--	x	NOT RUN	--	NOT RUN
Trichloronaphthalene		2	NOT RUN	--	--	--	NOT RUN	--	x (2)	NOT RUN	--	NOT RUN
Tetrachloronaphthalene		2	NOT RUN	--	--	--	NOT RUN	--	x	NOT RUN	--	NOT RUN
Benzene		1	NOT RUN	--	--	--	NOT RUN	--	--	NOT RUN	x	NOT RUN
Acenaphthylene or Biphenylene	 or 	1	NOT RUN	--	--	--	NOT RUN	--	--	NOT RUN	x	NOT RUN

C-2

FOOTNOTES

[a] Identifications are considered tentative because actual standards were not analyzed to confirm them. Other isomers are possible.

[b] Possible structures are presented. Other isomers are possible in some cases.

[c] Confidence factors:

1 = Spectral match found in EPA-NIH library.
2 = No library match found; manual spectral interpretation was performed with high confidence in results.
3 = No library match found; manual spectral interpretation yielded results which may be subject to error.

N/A = Not applicable.

[d] Results codes:

x = Compound was detected as a major thermal decomposition product.
xx = Compound was one of the largest peaks in the thermal decomposition run.
x (number) = More than one isomer of the given compound was detected. The number of isomers is given in parentheses.
xx (number) = More than one isomer of the given compound was detected and the summed peaks constituted one of the highest yield thermal decomposition products.
-- = Compound was not a major thermal decomposition product.

TABLE C-3. MAJOR THERMAL DECOMPOSITION PRODUCTS FROM COMPOSITE B SPIKED SLUDGE

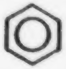
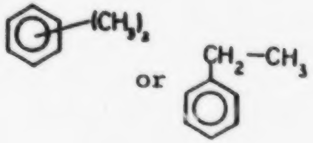
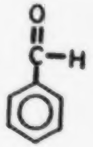
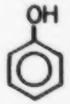
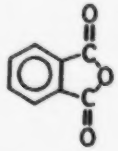
Tentative Identification[a]	Structure[b]	Confidence Factor[c]	600°C		650°C		750°C		800°C	
			N_2	Air	N_2	Air	N_2	Air	N_2	Air
Benzene and/or Isomer		1	x[d]	x	xx (2)	NOT RUN	xx (2)	NOT RUN	NOT RUN	xx
Xylene or Ethylbenzene		1	x	x (2)	xx		x (2)			--
Benzaldehyde		1	x	xx	x		x			--
Phenol		1	xx	x	xx		--			--
Phthalic anhydride		1	x	xx	x		--			--

TABLE C-3 (CONTINUED)

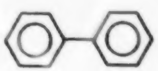
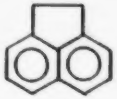
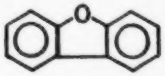
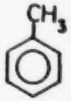
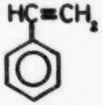
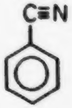
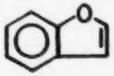
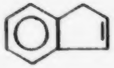
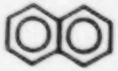
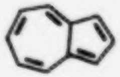
Tentative Identification[a]	Structure[b]	Confidence Factor[c]	600°C N_2	600°C Air	650°C N_2	650°C Air	750°C N_2	750°C Air	800°C N_2	800°C Air
Biphenyl or Acenaphthene	 or 	1	x	x	x	NOT RUN	x	NOT RUN	NOT RUN	--
Dibenzofuran		1	x	x	x		--			--
C_7-Alkene or C_7-Cycloalkane or C_6-Unsaturated Ketone	C_7H_{14} or $C_6H_{10}O$	2	--	--	x		--			--
Toluene		1	x	x	x		x			--
Styrene		1	--	--	x		x			--
Benzonitrile		1	--	x	x		x			--
Benzofuran		1	--	--	x		x			--
1H-Indene		1	--	--	--		x			--

TABLE C-3 (CONCLUDED)

Tentative Identification[a]	Structure[b]	Confidence Factor[c]	600°C		650°C		750°C		800°C	
			N_2	Air	N_2	Air	N_2	Air	N_2	Air
Naphthalene or Azulene	 or 	1	--	x	x	NOT RUN	x	NOT RUN	NOT RUN	--
C_9-Alkene or C_9-Cycloalkane	C_9H_{18}	2	--	x	--		--			--

C-3

FOOTNOTES

[a] Identifications are considered tentative because actual standards were not analyzed to confirm them. Other isomers are possible.

[b] Possible structures are presented. Other isomers are possible in some cases.

[c] Confidence factors:

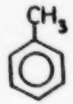
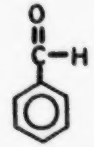
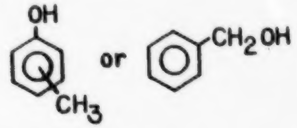
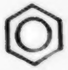
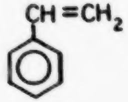
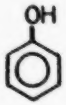
1 = Spectral match found in EPA-NIH library.
2 = No library match found; manual spectral interpretation was performed with high confidence in results.
3 = No library match found; manual spectral interpretation yielded results which may be subject to error.

N/A = Not applicable.

[d] Results codes:

x = Compound was detected as a major thermal decomposition product.
xx = Compound was one of the largest peaks in the thermal decomposition run.
x (number) = More than one isomer of the given compound was detected. The number of isomers is given in parentheses.
xx (number) = More than one isomer of the given compound was detected and the summed peaks constituted one of the highest yield thermal decomposition products.
— = Compound was not a major thermal decomposition product.

TABLE C-4. MAJOR THERMAL DECOMPOSITION PRODUCTS FROM COMPOSITE B SPIKE SOLUTION

Tentative Identification[a]	Structure[b]	Confidence Factor[c]	400°C		500°C		700°C		800°C	
			N_2	Air	N_2	Air	N_2	Air	N_2	Air
Toluene		1	x[d]	x	x	x	NOT RUN	x	x	NOT RUN
Benzaldehyde		1	x	xx	x	xx		xx	x	
Methylphenol or Benzyl alcohol		1	--	--	x	--		--	--	
Benzene		1	--	--	--	x		x	x	
Styrene		1	--	--	--	--		--	x	
Phenol		1	--	x	--	--		--	--	
Unknown	?	N/A	x	--	--	--		--	--	

C-4

FOOTNOTES

[a] Identifications are considered tentative because actual standards were not analyzed to confirm them. Other isomers are possible.

[b] Possible structures are presented. Other isomers are possible in some cases.

[c] Confidence factors:

1 = Spectral match found in EPA-NIH library.
2 = No library match found; manual spectral interpretation was performed with high confidence in results.
3 = No library match found; manual spectral interpretation yielded results which may be subject to error.

N/A = Not applicable.

[d] Results codes:

x = Compound was detected as a major thermal decomposition product.
xx = Compound was one of the largest peaks in the thermal decomposition run.
x (number) = More than one isomer of the given compound was detected. The number of isomers is given in parentheses.
xx (number) = More than one isomer of the given compound was detected and the summed peaks constituted one of the highest yield thermal decomposition products.
— = Compound was not a major thermal decomposition product.

TABLE C-5. MAJOR THERMAL DECOMPOSITION PRODUCTS FROM NONYLPHENOL SPIKED SLUDGE

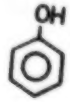
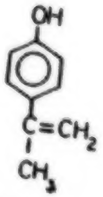
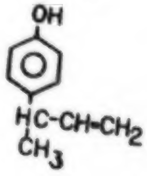
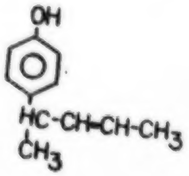
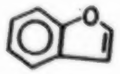
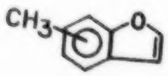
Tentative Identification[a]	Structure[b]	Confidence Factor[c]	Nitrogen Runs			Air Runs		
			550°C	700°C	850°C	475°C	625°C	650°C
Phenol		1	x[d]	x	--	x	x	--
C_3-Alkenylphenol[e]		2	xx	xx	--	xx	--	--
C_4-Alkenylphenol[e]		2	xx(3)	x	--	xx(3)	--	--
C_5-Alkenylphenol[e]		2	x(3)	--	--	x(2)	--	--
Benzofuran		1	x	x	x	--	x	x
Methylbenzofuran		1	x	x	--	x	x	x

TABLE C-5 (CONTINUED)

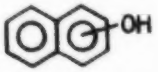
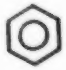
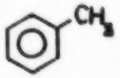
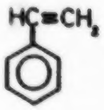
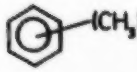
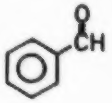
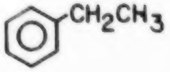
			Nitrogen Runs			Air Runs		
Tentative Identification[a]	Structure[b]	Confidence Factor[c]	550°C	700°C	850°C	475°C	625°C	650°C
Naphthalenol		1	x	x	--	--	--	--
Benzene or Isomer		1	--	x	x(2)	--	x(2)	x(2)
Toluene		1	--	x	x	--	x	x
Styrene		1	--	x(2)	x	--	x	x
Xylene		1	--	x(2)	x	--	--	--
Benzaldehyde		1	--	x	x	--	x	x
Ethylbenzene		1	--	x	x	--	--	--

TABLE C-5 (CONTINUED)

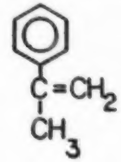
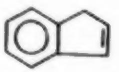
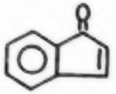
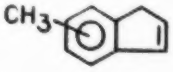
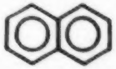
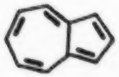
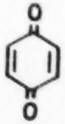
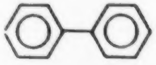
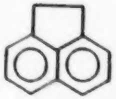
Tentative Identification[a]	Structure[b]	Confidence Factor[c]	Nitrogen Runs 550°C	Nitrogen Runs 700°C	Nitrogen Runs 850°C	Air Runs 475°C	Air Runs 625°C	Air Runs 650°C
C_3-Alkenylbenzene		2	--	x	x	--	--	--
1H-Indene		1	--	x	x	--	--	--
Inden-one		3	--	--	--	--	x	x
Methyl-1H-Indene		1	--	x	x	--	--	--
Naphthalene or Azulene	 or 	1	--	x(2)	x(2)	--	--	--
Quinone		1	--	--	--	--	xx	x
Biphenyl or Acenaphthene	 or 	1	--	--	x	--	--	--

TABLE C-5 (CONTINUED)

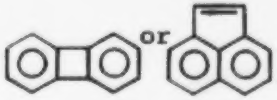
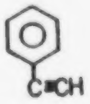
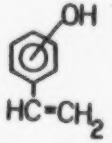
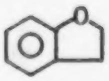
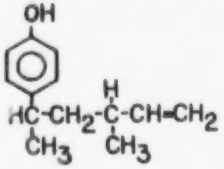
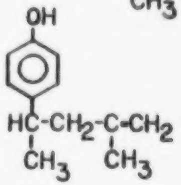
Tentative Identification[a]	Structure[b]	Confidence Factor[c]	Nitrogen Runs 550°C	 700°C	 850°C	Air Runs 475°C	 625°C	 650°C
Biphenylene or Acenaphthylene		1	--	x	x	--	--	--
Phenylacetylene		1	--	x	x	--	--	--
Hydroxystyrene or Dihydrobenzofuran	 or 	1	x	x	--	--	--	--
C_9-Alkene or C_9-Cycloalkane	C_9H_{18}	1	x(many)	--	--	--	--	--
C_7-Alkenylphenol[e]		2	x(3)	--	--	--	--	--
C_6-Alkenylphenol[e]		2	x(2)	--	--	--	--	--
Hexatriene or Isomer	$H_2C{=}CH{-}CH{=}CH{-}CH{=}CH_2$	1	--	x	--	--	--	--

TABLE C-5 (CONTINUED)

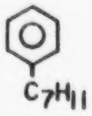
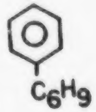
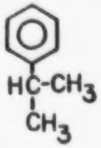
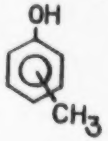
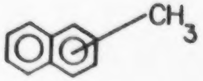
Tentative Identification[a]	Structure[b]	Confidence Factor[c]	Nitrogen Runs 550°C	Nitrogen Runs 700°C	Nitrogen Runs 850°C	Air Runs 475°C	Air Runs 625°C	Air Runs 650°C
Cyclohexadiene or C_6-ene-yne	C_6H_8	1	--	x	--	--	--	--
C_7-Alkadienylbenzene or C_7-Alkynylbenzene		3	--	x	--	--	--	--
C_6-Alkadienylbenzene or C_6-Alkynylbenzene		3	--	x	--	--	--	--
C_3-Benzene		1	--	x(2)	--	--	--	--
Methylphenol		1	--	x(2)	--	--	--	--
Cyclopentadiene or C_5-ene-yne	C_5H_6	1	--	--	x(2)	--	--	--
Methylnaphthalene		1	--	--	x	--	--	--

TABLE C-5 (CONTINUED)

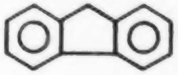
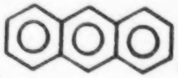
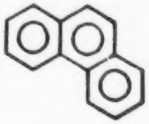
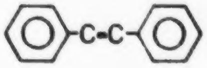
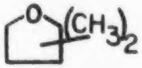
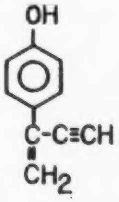
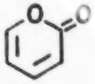
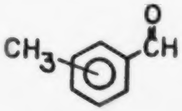
Tentative Identification[a]	Structure[b]	Confidence Factor[c]	Nitrogen Runs 550°C	Nitrogen Runs 700°C	Nitrogen Runs 850°C	Air Runs 475°C	Air Runs 625°C	Air Runs 650°C
9H-Fluorene		1	--	--	x	--	--	--
Anthracene, Phenanthrene, or Diphenylacetylene	 or  or 	1	--	--	x	--	--	--
Dimethyltetrahydrofuran		1	--	--	--	x	--	--
C_4-Alkenyl-ynyl-phenol		3	--	--	--	x	--	--
Alkene or Cycloalkane	?	1	--	--	--	--	x(many)	--
2H-pyran-2-one		1	--	--	--	--	--	x

TABLE C-5 (CONCLUDED)

Tentative Identification[a]	Structure[b]	Confidence Factor[c]	Nitrogen Runs			Air Runs		
			550°C	700°C	850°C	475°C	600°C	650°C
Methylbenzaldehyde		1	--	--	--	--	x	x

FOOTNOTES

[a] Identifications are considered tentative because actual standards were not analyzed to confirm them. Other isomers are possible.

[b] Possible structures are presented. Other isomers are possible in some cases.

[c] Confidence factors:

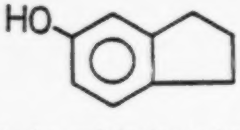
1 = Spectral match found in EPA-NIH library.
2 = No library match found; manual spectral interpretation was performed with high confidence in results.
3 = No library match found; manual spectral interpretation yielded results which may be subject to error.

N/A = Not applicable.

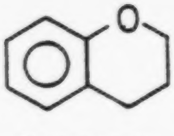
[d] Results codes:

x = Compound was detected as a major thermal decomposition product.
xx = Compound was one of the largest peaks in the thermal decomposition run.
x (number) = More than one isomer of the given compound was detected. The number of isomers is given in parentheses.
xx (number) = More than one isomer of the given compound was detected and the summed peaks constituted one of the highest yield thermal decomposition products.
— = Compound was not a major thermal decomposition product.

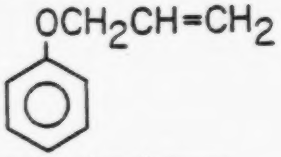
[e] Several additional isomers are possible for the alkenylphenols. For example alternative structures for C_3-alkenylphenol include:



hydroxydihydroindene



benzopyran



propenyloxybenzene

Addition of methyl, ethyl, etc., to these basic structures results in isomers equivalent to the higher alkenylphenols. The alkenylphenol isomers may vary in the position of the alkene double bond, as well as in the point of attachment of the alkenylgroup to the benzene ring. Definitive structural assignments cannot be made because insufficient information is present in the mass spectral data base.

TABLE C-6. MAJOR THERMAL DECOMPOSITION PRODUCTS FROM NONYLPHENOL SPIKE SOLUTION

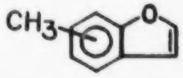
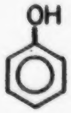
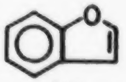
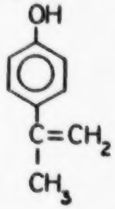
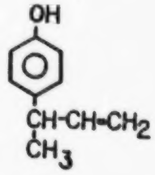
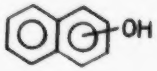
Tentative Identification[a]	Structure[b]	Confidence Factor[c]	475°C		525°C		650°C		700°C		750°C	
			N_2	Air	N_2	Air	N_2	Air	N_2	Air	N_2	Air
C_9-Alkene or C_9-Cycloalkane	C_9H_{18}	1	NOT RUN	x[d] Many Peaks	x Many Peaks	NOT RUN	--	NOT RUN	--	NOT RUN	--	NOT RUN
Methylbenzofuran		1		x	x		x		x		x	
Phenol		1		x	x		x		x		--	
Benzofuran		1		x	x		x		x		x	
C_3-Alkenylphenol[e]		2		xx	xx		xx		xx (2)		xx	
C_4-Alkenylphenol[e]		2		x (3)	xx (3)		x (3)		x (2)		--	
Naphthalenol		1		x	--		x		--		--	

TABLE C-6 (CONTINUED)

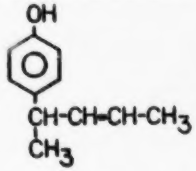
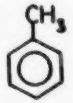
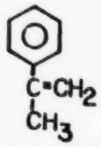
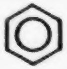
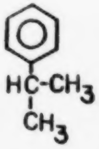
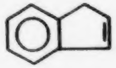
Tentative Identification[a]	Structure[b]	Confidence Factor[c]	475°C N_2	475°C Air	525°C N_2	525°C Air	650°C N_2	650°C Air	700°C N_2	700°C Air	750°C N_2	750°C Air
C_5-Alkenylphenol[e]		2	NOT RUN	x	x (3)	NOT RUN	--	NOT RUN	--	NOT RUN	--	NOT RUN
Toluene		1		--	--		x		x		x	
C_3-Alkenylbenzene		2		--	--		x		x		--	
Benzene		1		--	--		--		x		x	
C_3-Benzene		1		--	--		--		x (2)		x (2)	
1H-Indene		1		--	--		x		x		x	

TABLE C-6 (CONTINUED)

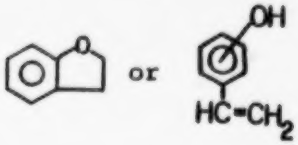
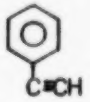
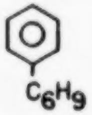
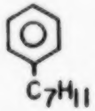
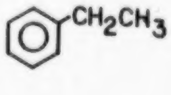
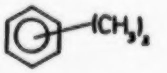
Tentative Identification[a]	Structure[b]	Confidence Factor[c]	475°C N_2	475°C Air	525°C N_2	525°C Air	650°C N_2	650°C Air	700°C N_2	700°C Air	750°C N_2	750°C Air
Dihydrobenzofuran or Hydroxystyrene		1	NOT RUN	--	--	NOT RUN	x	NOT RUN	x	NOT RUN	x	NOT RUN
Phenylacetylene		1		--	--		--		x		x	
C_6-Alkadienylbenzene		3		--	--		x		x		x	
C_7-Alkadienylbenzene		3		--	--		x		x		--	
Ethylbenzene		1		--	--		--		x		x	
Xylene		1		--	--		--		x		x	

TABLE C-6 (CONTINUED)

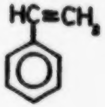
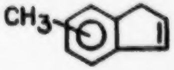
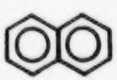
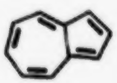
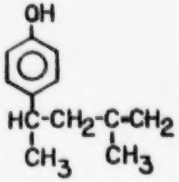
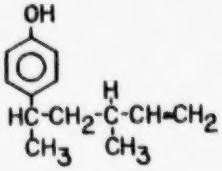
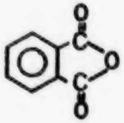
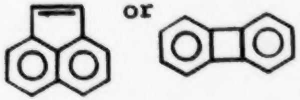
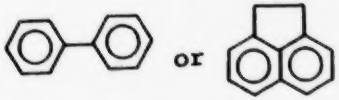
Tentative Identification[a]	Structure[b]	Confidence Factor[c]	475°C N_2	475°C Air	525°C N_2	525°C Air	650°C N_2	650°C Air	700°C N_2	700°C Air	750°C N_2	750°C Air
Styrene		1	NOT RUN	--	--	NOT RUN	x (2)	NOT RUN	x (2)	NOT RUN	xx (2)	NOT RUN
Methyl-1H-Indene		1		--	--		--		x (2)		x	
Naphthalene or Azulene	 or 	1		--	--		--		x		x (2)	
C_7-Diyne-ene or C_7-Cyclodiyne or C_7-Cyclodiene-yne	C_7H_6	2		--	--		--		x (2)		x (2)	
C_6-Alkenylphenol[e]		2		--	x (4)		--		--		--	
C_7-Alkenylphenol[e]		2		--	x (4)		--		--		--	

TABLE C-6 (CONCLUDED)

Tentative Identification[a]	Structure[b]	Confidence Factor[c]	475°C N_2	475°C Air	525°C N_2	525°C Air	650°C N_2	650°C Air	700°C N_2	700°C Air	750°C N_2	750°C Air
Phthalic anhydride		1	NOT RUN	--	x	NOT RUN	--	NOT RUN	--	NOT RUN	--	NOT RUN
Cyclohexadiene or C_6-ene-yne	C_6H_8	1		--	--		--		--		x (2)	
Acenaphthylene or Biphenylene		1		--	--		--		--		x	
Biphenyl or Acenaphthene		1		--	--		--		--		x	
Unknown(s)	?	N/A		--	--		--		x		x (2)	

FOOTNOTES

[a] Identifications are considered tentative because actual standards were not analyzed to confirm them. Other isomers are possible.

[b] Possible structures are presented. Other isomers are possible in some cases.

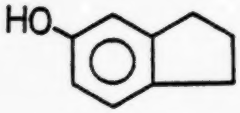
[c] Confidence factors:

1 = Spectral match found in EPA-NIH library.
2 = No library match found; manual spectral interpretation was performed with high confidence in results.
3 = No library match found; manual spectral interpretation yielded results which may be subject to error.
N/A = Not applicable.

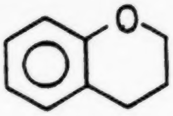
[d] Results codes:

x = Compound was detected as a major thermal decomposition product.
xx = Compound was one of the largest peaks in the thermal decomposition run.
x (number) = More than one isomer of the given compound was detected. The number of isomers is given in parentheses.
xx (number) = More than one isomer of the given compound was detected and the summed peaks constituted one of the highest yield thermal decomposition products.
— = Compound was not a major thermal decomposition product.

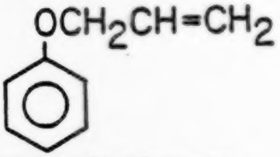
[e] Several additional isomers are possible for the alkenylphenols. For example alternative structures for C_3-alkenylphenol include:



hydroxydihydroindene



benzopyran



propenyloxybenzene

Addition of methyl, ethyl, etc., to these basic structures results in isomers equivalent to the higher alkenylphenols. The alkenylphenol isomers may vary in the position of the alkene double bond, as well as in the point of attachment of the alkenylgroup to the benzene ring. Definitive structural assignments cannot be made because insufficient information is present in the mass spectral data base.

TABLE C-7. MAJOR THERMAL DECOMPOSITION PRODUCTS FROM UNSPIKED SLUDGE

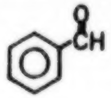
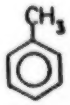
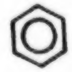
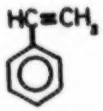
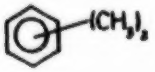
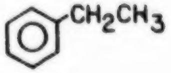
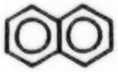
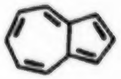
Tentative Identification[a]	Structure[b]	Confidence Factor[c]	500°C N_2	500°C Air	600°C N_2	600°C Air	650°C N_2	650°C Air	800°C N_2	800°C Air
Benzaldehyde		1	NOT RUN	x[d]	--	--	--	x	x	--
Toluene		1		--	xx	x	x	xx	x	--
Benzene		1		--	--	--	x	xx (2)	xx	x
Styrene		1		--	--	x	x	x	x	--
Xylene or Ethylbenzene	 or 	1		--	x	--	x	x	x	--
Naphthalene or Azulene	 or 	1		--	--	--	--	--	x	--
C_6-Alkene or C_6-Cycloalkane	C_6H_{12}	1		xx (2)	x	x	x (2)	--	--	--

TABLE C-7 (CONCLUDED)

Tentative Identification[a]	Structure[b]	Confidence Factor[c]	500°C N_2	500°C Air	600°C N_2	600°C Air	650°C N_2	650°C Air	800°C N_2	800°C Air
C_6-Unsaturated ketone or C_7-Alkene or C_7-Cycloalkane	$C_6H_{10}O$ or C_7H_{14}	1	NOT RUN	x	x	x	x	--	--	--
C_5-Diene or C_5-Cycloalkene	C_5H_8	1		--	x	--	--	--	--	--
C_6-Cyclodiene or C_6-ene-yne or C_6-Triene	C_6H_8	1		--	x	--	--	--	--	--
C_8-Alkene or C_8-Cycloalkane or C_7-Unsaturated ketone	C_8H_{16} or $C_7H_{12}O$	1		--	x	--	--	--	--	--
Unknown aliphatic hydrocarbon	?	N/A		x	x	--	--	--	--	--
Unknown alkene or cycloalkane	?	N/A		x (2)	xx (3)	x (2)	--	--	--	--
Miscellaneous unknown(s)	?	N/A		--	--	--	--	x (2)	--	--

C-7

FOOTNOTES

[a] Identifications are considered tentative because actual standards were not analyzed to confirm them. Other isomers are possible.

[b] Possible structures are presented. Other isomers are possible in some cases.

[c] Confidence factors:

1 = Spectral match found in EPA-NIH library.
2 = No library match found; manual spectral interpretation was performed with high confidence in results.
3 = No library match found; manual spectral interpretation yielded results which may be subject to error.

N/A = Not applicable.

[d] Results codes:

x = Compound was detected as a major thermal decomposition product.
xx = Compound was one of the largest peaks in the thermal decomposition run.
x (number) = More than one isomer of the given compound was detected. The number of isomers is given in parentheses.
xx (number) = More than one isomer of the given compound was detected and the summed peaks constituted one of the highest yield thermal decomposition products.
— = Compound was not a major thermal decomposition product.

TABLE C-8. COMPARISON OF THERMAL REACTION PRODUCTS FOR COMPOSITE A SPIKE SOLUTION VERSUS SPIKED SLUDGE

	500°C, N_2		500°C, Air		650°C, Air		800°C, N_2	
Tentative Identification[a]	Spike Solution	Spiked Sludge	Spike Solution	Spiked Sludge	Spike Solution	Spiked Sludge	Spike Solution	Spiked Sludge
9H-Carbazole	x[b]	--	x	x	--	--	xx	x
Chlorocyclopentadiene	x(2)	x(2)	xx(2)	--	--	--	--	--
Tetrachlorofuran	--	--	x	x	x	--	--	--
Trichlorodihydronaphthalene	--	--	x	x	--	--	--	--
Dichloroacetylene	--	--	--	--	x	--	--	--
Tetrachloropropyne	--	--	--	--	x	--	--	--
Pentachloronaphthalene	x	--	--	--	--	--	x	--
Biphenyldicarbonitrile	--	--	--	--	x	--	--	--
Diphenylamine or Aminobiphenyl	xx	xx	--	xx	--	--	--	--
Hexachlorodihydronaphthalene	x	--	--	--	--	--	--	--
Hexachloromethanocyclohexene	x	--	--	--	--	--	--	--
Benzonitrile	--	--	--	--	--	x	x	x
Naphthalene or Azulene	--	--	--	--	--	--	x	x
Tetrachlorobenzene	--	--	--	--	--	--	x	x
Pentachlorobenzene	--	--	--	--	--	--	x	--
Trichloronaphthalene	--	--	--	--	--	--	x(2)	--
Tetrachloronaphthalene	--	--	--	--	--	--	x	--
Benzene	--	--	--	--	--	x	--	xx
Toluene	--	--	--	--	--	x	--	x
Styrene	--	--	--	--	--	x	--	x
Cyclopentadiene or C_5-ene-yne	--	--	--	--	--	--	--	x

TABLE C-8(CONCLUDED)

Tentative Identification[a]	500°C, N_2 Spike Solution	 Spiked Sludge	500°C, Air Spike Solution	 Spiked Sludge	650°C, Air Spike Solution	 Spiked Sludge	800°C, N_2 Spike Solution	 Spiked Sludge
1H-Indene	--	--	--	--	--	--	--	x
Trichlorobenzene	--	--	--	--	--	--	--	x

---

[a] Identifications are considered tentative because actual standards were not analyzed to confirm them. Other isomers are possible.

[b] Results codes:

x = compound was detected as a major thermal decomposition product.
xx = compound was one of the largest peaks in the thermal decomposition run.
x(number) = more than one isomer of the given compound was detected. The number of isomers is given in parentheses.
xx(number) = more than one isomer of the given compound was detected and the summed peaks constituted one of the highest yield thermal decomposition products.
-- = compound was not a major thermal decomposition products.

TABLE C.9

MAJOR COMPOUNDS DETECTED FROM DECOMPOSITION OF COMPOSITE A SPIKING SOLUTION AND SPIKED SLUDGE AT 500°C IN N_2 (HIGHER INSERTION REGION TEMPERATURE)

Compound[a]	Peak Intensities[b] Spiking Solution[c]	 Spiked Sludge[d]
Chlorocyclopentadiene or chloropenten-yne (2 isomers)	3.7×10^3	NA[f]
Diphenylamine[e]	2.3×10^4	5.8×10^4
Pentachlorophenol[e]	2.5×10^4	6.8×10^3
9H-Carbazole	1.0×10^3	ND[g]
Pyrene[e]	8.1×10^4	4.0×10^4
Pentachloronaphthalene	5.6×10^3	ND
Hexachlorodihydronaphthalene	1.7×10^3	ND
Hexachloromethanocyclohexene or isomer	7.0×10^2	ND
Phthalic anhydride	ND	4.4×10^3
C_{14}-alkene or cycloalkane	ND	6.7×10^3
C_{15}-alkene or cycloalkane	ND	8.5×10^3
C_{16}-alkene or cycloalkane (2 isomers)	ND	1.7×10^4
C_{17}-alkene or cycloalkane	ND	5.7×10^3
C_{19}-alkene or cycloalkane (2 isomers)	ND	1.7×10^4
Dodecylbenzene	ND	7.9×10^3
Fluoranthene	ND	8.1×10^3
Cholest-ene (10 isomers)	ND	2.2×10^5
Cholest-ene-dione or cholest-dien-ol (3 isomers)	ND	5.0×10^4
Epoxy cholestane	ND	9.4×10^3

FOOTNOTES FOR TABLE C.9

[a] Tentative mass spectral identifications.

[b] Peak intensities are supplied for semi-quantitative comparison of relative concentrations. These numbers provide order-of-magnitude estimations of relative peak heights, and should not be construed as more accurate than this.

[c] Four-component mixture containing diphenylnitrosamine, pentachlorophenol, heptachlor, and pyrene.

[d] Municipal sludge spiked at ~1000 µg/g (ppm) with the four-component mixture described in footnote c.

[e] Parent or spike material (or primary decomposition product in case of diphenylamine).

[f] NA=not analyzed because initial GC column temperature was too high to trap this compound. Initial temperature was -40°C for spiking solution and 30°C for spiked sludge. Spiked sludge could not be analyzed at -40°C due to freezing of water in column.

[g] ND=not detected, with a detection limit ~5.0×10^2.

TABLE C.10

MAJOR COMPOUNDS DETECTED FROM DECOMPOSITION OF COMPOSITE A SPIKING SOLUTION AND SPIKED SLUDGE AT 800°C IN N_2 (HIGHER INSERTION REGION TEMPERATURE)

Compound[a]	Peak Intensities[b]	
	Spiking Solution[c]	Spiked Sludge[d]
Benzonitrile or isocyano-benzene	2.9×10^3	NA[f]
Naphthalene or azulene	1.9×10^3	7.1×10^3
Tetrachlorobenzene	5.2×10^2	6.7×10^3
Pentachlorobenzene	1.2×10^3	3.5×10^3
Trichloronaphthalene (3 isomers)	2.7×10^3	3.5×10^3
9H-Carbazole	7.4×10^3	2.0×10^4
Tetrachloronaphthalene	3.0×10^3	2.2×10^3
Pyrene[e]	6.3×10^4	$>6.4 \times 10^4$
Pentachloronaphthalene	1.7×10^3	3.2×10^3
Methylnaphthalene (2 isomers)	ND[g]	7.1×10^3
Acenaphthylene and biphenylene	ND	9.4×10^3
Diphenylamine[e]	ND	1.8×10^4
Anthracene or phenanthrene	ND	9.9×10^3
Aromatic compound with possible formula $C_{15}H_{10}$	ND	8.1×10^3
Trichlorobenzene (2 isomers)	ND	4.3×10^3
Quinoline or isoquinoline	ND	7.7×10^2
Acenaphthylene or biphenylene	ND	2.4×10^3
Biphenyl	ND	3.0×10^3
Naphthalene carbonitrile (2 isomers)	ND	4.0×10^3
9-H-Fluorene or isomer (2 peaks)	ND	6.6×10^3
Tetrachlorostyrene	ND	2.0×10^3
Tetrachlorodihydronaphthalene	ND	3.1×10^3
Biphenyl dicarbonitrile	ND	5.9×10^3
Pentachloronaphthalene	ND	3.0×10^3

FOOTNOTES FOR TABLE C.10

[a] Tentative mass spectral identifications.

[b] Peak intensities are supplied for semi-quantitative comparison of relative concentrations. These numbers provide order-of-magnitude estimations of relative peak heights, and should not be construed as more accurate than this.

[c] Four-component mixture containing diphenylnitrosamine, pentachlorophenol, heptachlor, and pyrene.

[d] Municipal sludge spiked at ~1000 μg/g (ppm) with the four-component mixture described in footnote c.

[e] Parent or spike material (or primary decomposition product in case of diphenylamine).

[f] NA=not analyzed because initial GC column temperature was too high to trap this compound. Initial temperature was -40°C for spiking solution and 30°C for spiked sludge. Spiked sludge could not be analyzed at -40°C due to freezing of water in column.

[g] ND=not detected, with a detection limit ~5.0×10^2.

TABLE C.11

MAJOR COMPOUNDS DETECTED FROM DECOMPOSITION OF COMPOSITE A SPIKING SOLUTION AND SPIKED SLUDGE AT 1000°C IN N_2 (HIGHER INSERTION REGION TEMPERATURE)

Compound[a]	Peak Intensities[b]	
	Spiking Solution[c]	Spiked Sludge[d]
Benzene	2.0×10^{2}	NA[f]
Benzonitrile or isocyano-benzene	2.9×10^{2}	NA
Acenaphthylene or biphenylene	3.3×10^{2}	2.5×10^{3}
Pyrene[e]	7.3×10^{3}	2.7×10^{2}
Naphthalene or azulene	ND[g]	1.8×10^{3}
9H-Fluorene	ND	1.8×10^{2}
Anthracene or phenanthrene	ND	4.4×10^{2}
Fluoranthene	ND	1.1×10^{2}

---

[a] Tentative mass spectral identifications.

[b] Peak intensities are supplied for semi-quantitative comparison of relative concentrations. These numbers provide order-of-magnitude estimations of relative peak heights, and should not be construed as more accurate than this.

[c] Four-component mixture containing diphenylnitrosamine, pentachlorophenol, heptachlor, and pyrene.

[d] Municipal sludge spiked at ~1000 µg/g (ppm) with the four-component mixture described in footnote c.

[e] Parent or spike material (or primary decomposition product in case of diphenylamine).

[f] NA=not analyzed because initial GC column temperature was too high to trap this compound. Initial temperature was -40°C for spiking solution and 30°C for spiked sludge. Spiked sludge could not be analyzed at -40°C due to freezing of water in column.

[g] ND=not detected, with a detection limit ~5.0×10^{2}.

APPENDIX D

OH ELEMENTARY REACTION KINETICS ERROR ANALYSIS

The time delay program that runs the lasers during a kinetic determination allows the user to choose the number of times the lasers will be fired for each increment in the time delay interval. This results in a number of OH signal values for each delay time. Thus, error analysis can be used to determine the precision of the experimental data. This appendix will present a description of the methods used for the analysis of the experimental data.

Two equations are used to calculate the rate constants from the experimental data:

$$\frac{[OH]_t}{[OH]_o} = e^{-k't} \qquad (1)$$

$$k' = kA_o + k_d \qquad (2)$$

where: $[OH]_t/[OH]_o$ is the fraction of OH remaining at time t (f_r), k' is a first order rate constant, A_o is the initial concentration of the organic compound, k_d is the rate constant for diffusion of the reaction volume, and k is the rate constant of OH attack on the organic compound. Rearranging these equations results in the following working forms for the error analysis:

$$k' = \frac{\ln f_r}{t} \qquad (3)$$

$$k = \frac{k'k_d}{A_o}. \qquad (4)$$

The uncertainty in the rate constant k is dependent on the uncertainty in k' and k_d. The standard deviation for k' is given as:

$$\sigma_{k'} = -k' \left[\left(\frac{\bar{\sigma} f_r}{f_r \ln f_r} \right)^2 + \frac{\sigma t^2}{t^2} \right]^{1/2} \qquad (5)$$

where k' is the least squares slope of ln f_r versus t, $\bar{\sigma} f_r$ is the average standard deviation of the OH signal, f_r is the PMT signal, σ_t is the standard deviation in the time increment, and t is the time increment.

For each time increment in the delay interval, σf_r is calculated. This is divided by the mean OH signal for that increment times the logarithm of that mean, and tabulated.

An average value is obtained, squared, and used as the first term in brackets in Equation (5). Similarly, σ_t/t is calculated, tabluated, and averaged. This is made possible as it has been determined that the time delay generator is accurate to within 1 μs in 100 μs. The best fit slope through the data is then calculated and used for k'. Thus, a value for $\sigma_{k'}$ is known for each data run.

Using Equation (2), the uncertainty in k is given as:

$$\sigma_k = \left[\frac{1}{A_o^2} \left(\sigma_{k'}^2 + \sigma_{k_d}^2 \right) \right]^{1/2} \qquad (6)$$

where A_o is the initial concentration of the organic compound, σ_k is the standard deviation of k', and k_d is the standard deviation of k_d. For this analysis, σ_{k_d} is set equal to $\sigma_{k'}$. Thus:

$$\sigma_k = \sqrt{2} \, \frac{\sigma_{k'}}{A_o}. \qquad (7)$$